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Cellulose acetate production from Finnish hardwood and softwood dissolving pulp

Master´s Programme in Chemical, Biochemical and Materials Engineering

Major in Biomass Refining

Master's thesis for the degree of Master of Science in Technology submitted for inspection, Espoo, 7th of November, 2019.

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Abstract

Cellulose acetate pulp was produced from viscose-grade, unbleached and bleached hardwood dissolving pulps and bleached softwood dissolving pulp. The raw materials were purified by cold caustic extraction and elemental-chlorine free bleaching. Initially, pulp purification was optimized for all of the pulps. The unbleached hardwood pulp was purified with cold caustic extraction, bleached with D_0-EOP-D_1-P bleaching sequence and then acetylated. The same acetylation and bleaching conditions were applied for all the samples. The resulting cellulose acetate quality had a complex relation to the quality of raw material and extent of purification. The most cost-effective CCE was obtained with 5% consistency, 30 min reaction time, and 30 °C 70 g/L NaOH. Transmission and yellowness of the cellulose acetate solution for the most successful hardwood sample were 50 % and 0.29 respectively and for the most successful softwood sample 40 % and 0.26. The corresponding values for cellulose acetates prepared from the commercially available acetate-grade pulps were 78 % and 0.27 for hardwood and 73 % and 0.35 for softwood. The produced cellulose acetate quality was mediocre even when the purification was on an excellent level due to several factors affecting the acetylation process; some of the main reasons are probably extensive degradation of the fibers due non-optimal raw material with too low degree of polymerization. The result of the experimental work was the production of a low-quality acetate pulp from hardwood and softwood viscose pulps by cold caustic extraction and, in the case of unbleached pulp, by additional ECF bleaching.

Keywords Cellulose acetate, Cold Caustic Extraction, Dissolving pulp, ECF Bleaching

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Tiivistelmä

Selluloosa-asetaattia valmistettiin kylmävalkaistusta ja ECF-valkaistusta keskilaatuisesta liukosellusta. Kaiken kaikkiaan kolmea puuraaka-ainetta käytettiin: Valkaisematonta ja valkaistua lehtipuuliukosellua sekä valkaistua havupuuliukosellua. Selluloosan puhdistus optimoitiin kaikille massoille. Valkaisematon lehtipuuliukosellu puhdistettiin kylmäalkaliuutolla, valkaistiin D_0-EOP-D_1-P valkaisusekvenssillä ja asetyloitiin Testovan (2015) prosessilla. Asetylointi- ja valkaisuolosuhteet pidettiin samana läpi prosessin. Valmistetun selluloosa-asetaatin laadun huomattiin olevan monimutkaisessa suhteessa raaka-aineen laadun ja puhdistuksen kattavuuden kanssa. Parhaan puhdistuksen, ominaisuuksien ja hinnan suhteen 70 g/l natriumhydroksidiliuoksen havaittiin olevan optimi kylmäalkaliuutossa. Keltaisuus ja sakeudesta mitattava valonläpäisevyys parhaiten onnistuneille näytteille olivat lehtipuunäytteelle 50% ja 0.29 ja havupuunäytteelle 40% ja 0.26. Markkinoilta ostetusta asetaattilaadun liukosellusta valmistetun selluloosa-asetaatin vastaavat arvot olivat lehtipuunäytteelle 78% ja 0.27 ja havupuunäytteelle 73% ja 0.35. Asetylointitulokset puhdistetusta sellusta olivat heikkolaatuisia, vaikka puhdistaminen oli erinomaisella tasolla. Tämä johtuu useiden vaikuttavien tekijöiden summasta, suurimpina todennäköisesti kuitujen liiallinen pilkkoutuminen ja reaktiivisuuden heikentyminen. Kuitujen pilkkoutuminen johtui todennäköisesti raaka-aineen alhaisesta polymeroitumisasteesta. Tämän työn kokeellisen osuuden tuloksena valmistettiin heikkolaatuista asetaattisellua viskoosilaatuisesta havu- ja lehtipuusellusta kylmäalkaliuuton avulla. Valkaisematon lehtipuusellu myös valkaistiin ECF-valkaisulla.

Avainsanat Selluloosa-asetaatti, Kylmäalkaliuutto, Liukosellu, ECF-valkaisu

Preface

My thesis was conducted within Department of Biosystems and Bioproducts in cooperation with Stora Enso. I am thankful for the hard work and dedication of the department staff and group members as well as the endless support from the Imatra Research Center. The experience would not have been the same without the support and morale boost of the people around me. I sincerely thank you all!

The path may not always been the easiest for me, but I am honored and thankful for the possibility to work with my supervisor Professor Herbert Sixta. I am in awe of his ability to transfer complex knowledge onwards in understandable and compact manner. This could not only be seen and experienced through his guidance, but as well from the vast amount of knowledge, which had been acquired by Huy Quang Lê and Marina Ståhl who both helped and supported me greatly throughout the project. I feel warm embrace when working in all of their care.

I would not be able to pass on this preface, if I did not thank everybody from the Puunjalostajakilta, Kemistikilta, Vuorimieskilta and Prosessiteekkarit for their tips, support and stress relieving company.

Finally, I would like to thank the most important people in my life for giving me the possibility to even be in this point, my family. I cannot even put to words how grateful I am for their support, encouragement and care. I am not a person who says this enough but thank you for everything; you are the most valuable I have.

Espoo, 30.6.2019

Risto Hertzberg

List of Abbreviations

Adt = Air Dry Ton

AS = Acid sulfite pulping

BB = Big Batch

BS = Brown stock

CCE = Cold Caustic Extraction

CA = Cellulose Acetate

CDA = Cellulose Diacetate

ClO_2 = Chlorine Dioxide

CTA = Cellulose Triacetate

DP = Dissolving Pulp

DoP = Degree of Polymerization

ECF = Elemental Chlorine Free

GTA = Glucomannan Triacetate

Odp = oven-dried pulp

PHK = Prehydrolysis kraft

HA = Hemicellulose acetate

HW = Hardwood

HWBL = Hardwood bleached dissolving pulp

HWBS = Hardwood brownstock

HWC = Commercial hardwood acetate pulp

Mw = Molecular weight

NaOH = Sodium Hydroxide

SO_2 = Sulfur dioxide

SW = Softwood

SWBL = Softwood bleached dissolving pulp

SWC = Commercial softwood acetate pulp

Wt-% = Weight percentage

Contents

1 Introduction

1.1 Structure

This thesis is divided into different sections to answer the research questions in a logical and systematic way. The first part of the thesis is the introduction to the topic and the relevant background to validate the thesis and subject. The literature review begins by covering the fundamental knowledge, before presenting also relevant industrial background, standard analyses, the commercial aspect and lastly, the future prospects of the topic. In the experimental part, the plan is presented in the beginning, and the initial settings are introduced. The laboratory work is covered in detail, the results are presented for further discussion, and finally, conclusions are drawn.

1.2 Enocell Mill & Stora Enso

The Enocell mill in Uimaharju is well-established pulp mill owned by Stora Enso Oyj. Stora Enso is a Finnish-Swedish multinational co-operation company with employees in 35 different countries and market value of ca. 12 B € (2018). The mill has two fiberlines with combined annual pulp production capacity of 475 Adt and the main products are hardwood (HW) pulp, and bleached softwood (SW) pulp. The company's strategy is to invest in novel sustainable ways of making products from renewable resources for applications around the world.

1.3 Background

Products from sustainable and renewable raw materials becoming more popular among consumers, while also being economically and environmentally feasible options for the companies in the forest-based industries. The forest-based industry has been in transition phase as the demand for traditional paper is declining while other wood-based products, such as bioplastics, biofuels, medical and hygiene products are gaining market share. Cellulose, cellulose derivatives, polysaccharides and their derivatives are in a transition phase from traditional bulk products to highly customized novel products. The chemistry

of lignocellulosic materials has been studied extensively over the past century. The last decade witnessed several breakthroughs, which together with recent commercial success of the sector have triggered another renaissance in the cellulose derivatives research (Klemm, 2005). Some of the main reasons for the increasing popularity of cellulose-based products are the readily available infrastructures, the truly renewable nature and the vast potential of cellulose modification. Increasing consumption of single-use short life cycle products are increasing the environmental burden, to which novel bio-based products can be the answer. The stress of production can thus be shifted from more undeveloped areas to industrially more sustainable areas. (Testova, 2014a)

Cellulose acetate (CA) is the most industrially relevant cellulose ester derivative with annual production of roughly 80,000 tons. Paul Schützenberger discovered CA synthesis already in 1865 and the first commercial CA yarn was produced in 1921. CA products were, at first, mainly textile products, but then expanded to films, eyeglass frames, in blend with other textiles, tows and filaments. (Alén, 2011; Anon, 2014)

1.4 Aim of the work and research questions

The main purpose of this Master's thesis is to explore possibilities regarding the production and properties of CA from the provided dissolving pulp (DP). The methods of the work aim to fulfill a good and necessary scientific approach to research, as well as to contribute towards the completion of the Master's degree.

Research questions for this thesis revolve around the production of CA from viscose grade DP. The broadest research questions are the following:

1. Can the supplied pulp be converted into acetate-grade pulp?
2. What is the effect of the CCE treatment to the pulp properties?

To answer these questions, one needs to know what the evaluation criteria are and how to achieve those. There are actually not widely accepted and definitive criteria regarding the quality of pulp in this sense. However, some of the most important factors are narrow molecular mass distribution, low degree of oxidation, pulp purity, meaning that the amount of lignin, hemicelluloses and other non-cellulosic impurities should be as low as possible to achieve the highest quality CA.

LITERATURE REVIEW

2 Cellulose

Cellulose is a linear, semi-crystalline homo-polysaccharide of β-D-glucopyranose units, which are linked through β-(1-4)-glucosidic bonds. Glucose, not cellobiose, is recently identified as the repeating unit of cellulose. (French, 2017) Most chemical modifications of cellulose are made on the three hydroxyl groups of glucose. (Qiu, 2013; Wilson, 1986) The cellulose macrostructure consists of crystalline and amorphous regions, which form long, linear and rigid chain-structures, with a tendency of forming inter- and intramolecular hydrogen bonds as seen from Figure 1. This inter- and intramolecular hydrogen bonding, among other properties, results in a strong, flexible structure and an insolubility to most solvents. Hydrogen bonding networks contribute to the partially crystalline structure of cellulose. Cellulose structure has several different orientations from cellulose I to cellulose IV, from which cellulose III & IV are reversible forms of cellulose I and II. Cellulose I (parallel chain orientation) is the native form of cellulose. Cellulose II (anti-parallel chain orientation) is prevalent in regenerated or alkali-treated cellulose and has more complex hydrogen bonding, thus they have lower reactivity, and also the transformation from cellulose I to cellulose II is irreversible. (Qiu, 2013; Klemm, 2005; Wilson, 1986)

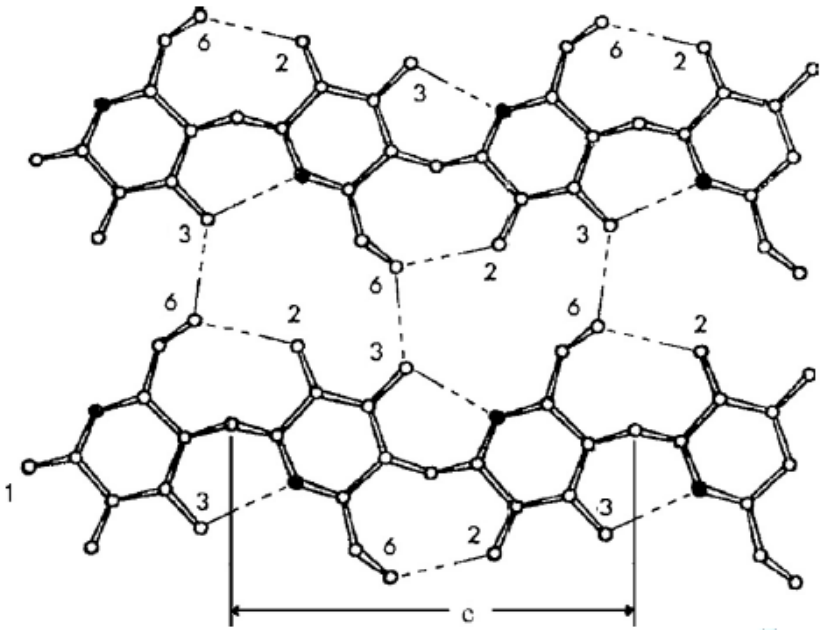

Figure 1. Cellulose chain structure with inter- and intrachain hydrogen bonding. (Adapted from Rowell, 2005)

The supramolecular structure (Figure 2) of cellulose fiber is based on the alignment and organization of multiple bundled cellulose microfibrils, which consists of multiple elementary fibrils, which in turn are long chains of glucose units. However, protective polysaccharide chains, namely hemicelluloses and lignin, are surrounding the microfibrils. (Olszewska, 2013) The amorphous regions are more prone to chemical modifications, but to allow access to the crystalline areas of the cellulose, the protective layer and the highly ordered structure of the microfibrils requires weakening or complete dissolution. Otherwise, most of the reactions would be limited to the amorphous regions, even in more intense reaction conditions. (Chunilall, 2013)

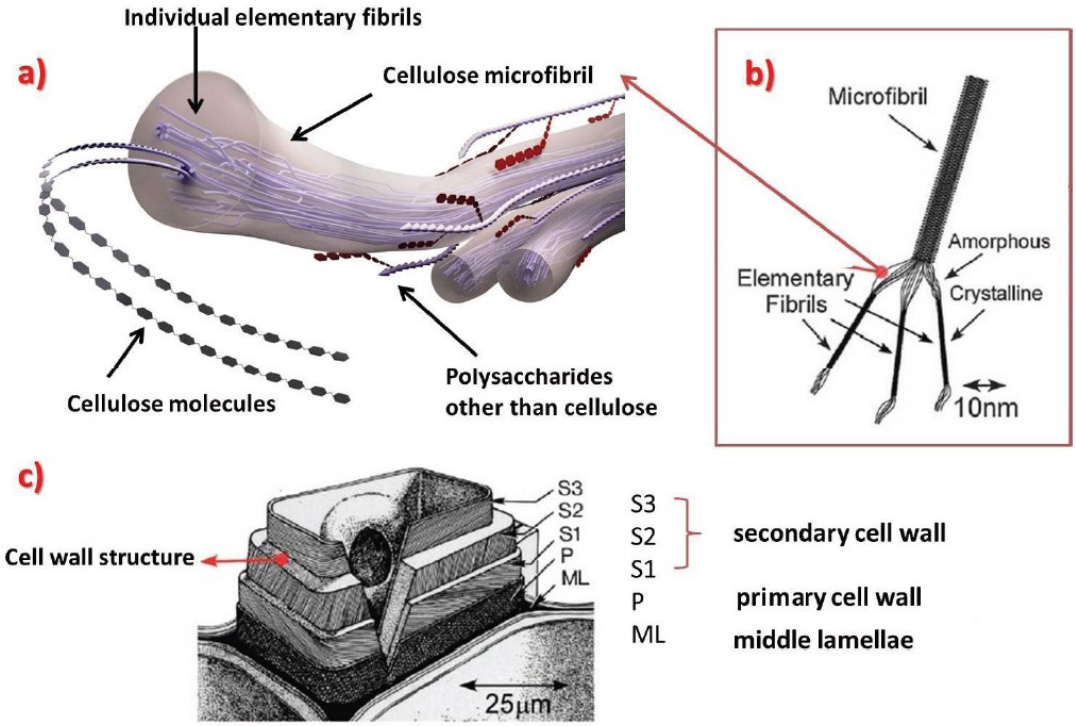

Figure 2. Hierarchical structure of the cellulose microfibrils and elementary fibrils (a, b) with fiber structure (c). (Adapted from Olszewska, 2013)

Cellulose has several valuable qualities to be utilized in industrial processes and in chemical applications: it is colorless, odorless and nontoxic; and it is a solid polymer with high mechanical strength, hydrophilicity, biocompability, thermostabilization capability, high sorption capacity and fine-tunable optical properties. (Qiu, 2013) One of the most

important properties of cellulose, when used as raw material for chemical modifications, is the number of glucose units in the chain, namely the degree of polymerization (DoP). Due to the heterogeneous nature of biomaterial, the cellulose chains are of different length, so the DoP of cellulose is an average value. DoP has correlation with strength and processability of the pulp. Average DoP of native cellulose is considered to be roughly 15,000 units. For reference, the average DoP of cellulose ester product DoP can be as low as 200. (Wilson, 1986)

2.1 Principle of cellulose derivatives production and functionalization

The utilization potential of cellulose in chemical modification is determined by the functionalization of the hydroxyl groups of the glucose unit. There are three main hydroxyl groups, which are classified as primary, which is located in C-6 and secondary, which are located in C-2 and C-3 (Figure 3). They are susceptible to all modifications for alcoholic hydroxyl groups, such as esterification, etherification and oxidation reactions. The most commercially relevant applications are based on the esterification and etherification reactions of the cellulose. (Qiu, 2013; Strunk, 2012; Klemm, 2005)

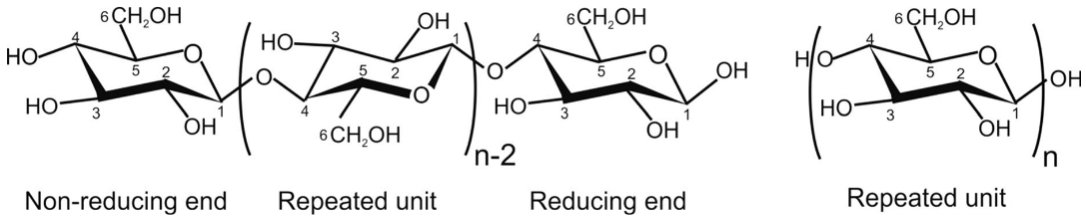

Figure 3. Segment of cellulose chain with different units (left) and the repeated unit (right). (French, 2017)

While the cellulose structure is unique and seemingly simple, the modification potential of cellulose is significant. In DP applications, the cellulose fraction is greater, which decreases the potential of side reactions and allows a better reaction environment for the modification of the cellulose chain. The functional hydroxyl groups can be chemically modified into, for example ethers, nitrates or acetates with established processes. Combined physical and chemical treatments can also significantly affect the properties of

the pulp to form e.g. nanofibrillated cellulose (NFC). (Figure 4). The potential is largely based on the accessibility of the functional hydroxyl groups. The accessibility is related to the swelling ability of the cellulose structures, which is greatly impacted by the water content and the DoP. DoP affects the reactivity, which is proportional to the extent of cellulose modification reactions. The supramolecular structure of cellulose (e.g. crystallinity) is determined by two distinctive features: the hydrogen bonding, and surface hydrophilicity. The resulting macromolecular structure and surface chemistry attribute the water-insolubility of cellulose. These properties greatly affect the swelling capability of cellulose stuctures. Celulose crystallinity also gives indications of the cellulose reactivity as the hydroxyl groups are more readily available in the amorphous regions. (Varshney, 2011; Klemm, 2005; Wilson, 1986) However, in practice the accessibility has to be compromised to achieve higher purity and DoP due to the unselectivity of the purification methods. The interrelated properties of the pulp are the greatest challenges in the production of high-purity cellulose. (Testova, 2014)

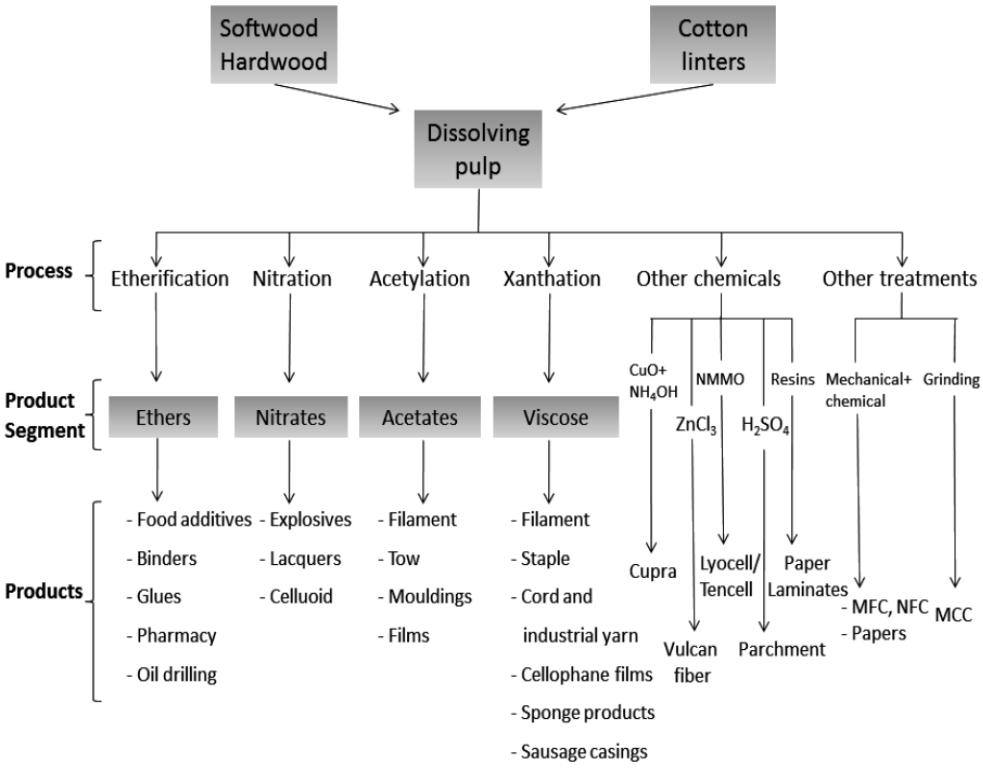

Figure 4. Cellulose derivatives and products categorized by the reaction. (Strunk, 2012)

2.1.1 Acetylation step

Acetylation is performed as a catalyzed liquid phase reaction combined with a pretreatment step. (Alén, 2011) Perchloric acid and zinc chloride have been used as catalysts, but sulfuric acid is the most available, safe and convenient (Sjöström, 1993). The main reaction with pulp for acetic anhydride is the esterification of the accessible hydroxyl groups, with a side product of acetic acid. The acetylation reaction (Figure 5) is a single-site reaction, meaning that only one acetyl group at a time is substituting the hydroxyl groups and polymerization does not occur. (Alén, 2011) The purpose of acetic acid pretreatment with sulfuric acid is for fibers swelling and reactivity enhancing for the following acetylation. (Sjöström, 1993)

$$C_6H_7O_2(OH)_3]_n + 3\ n\ (CH_3CO)_2O \rightarrow [C_6H_7O_2\ (OCOCH_3)_3]_n + 3\ n\ CH_3COOH$$

Figure 5. Acetylation reaction scheme. (Modified from Testova, 2014)

2.2 Cellulose acetate

The term CA is a commonly used to describe cellulose (mono)acetate (CMA), cellulose diacetate (CDA) and cellulose triacetate (CTA). CTA (Figure 6) is synthesized by the complete acetylation of high purity cellulose, while the CDA and CMA can be produced from CTA by partial hydrolysis. Traditional requirements for the commercial raw materials are high-quality cellulose with α-cellulose content of over 95 % and hemicellulose content of lower than 2.8 %, as demonstrated in Table 1. Due to the high purity requirements, CA is usually prepared from high-quality DP. DP raw material can be produced from SW, HW or a mixture of both. The production of the DP varies depending on the raw material. (He, 2009; Saka, 2004) The most common industrial processes for the DP production from wood are prehydrolysis kraft (PHK) and acid sulfite (AS) processes. (Sixta, 2006) The pulping process itself is not too relevant as the common requirement for the cooking is the removal of lignin and hemicellulose from pulp. However, PHK yields slightly higher alpha cellulose content for wood pulp, making it a more suitable process. (Saka, 2004)

Table 1. Typical minimum requirements for high-quality acetate-grade pulps (Alén, 2011; Sixta, 2006; Sjöström, 1993)

Properties	**Value**
Ash	< 0.07 %
Metal content	< 10 ppm
Extractives (ether)	< 0.15 %
Hemicellulose	< 1.5 %
Kappa number	< 0.2
PDI	< 3.2
Intrinsic viscosity	650-900 mL/g
Brightness	> 92 %
R_{10} / R_{18}	97.7 % / 98.2 %

It is possible to adjust the CA process to utilize low-grade DP (α-cellulose content <90 %, hemicellulose content >10 %). However, hemicelluloses form hemicellulose acetates (HA) during acetylation, which result in anomalies in filterability properties, turbidity or viscosity measurements in the CTA process. Additionally, HA may interact with glucomannan triacetate (GTA) and CTA, forming aggregates. (Saka, 1997) These anomalies result in low-quality CA. Therefore, lowering the quality of raw materials may significantly increase the raw material usage, the complexity of the process and purification requirements to achieve same yield as with purer pulp. (He, 2009; Saka, 1997)

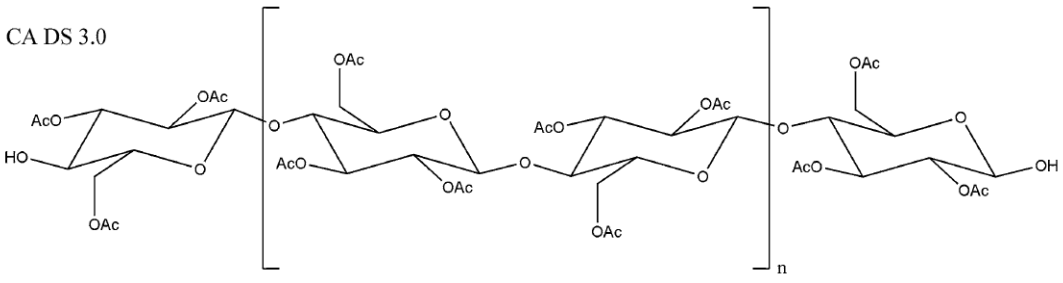

Figure 6. The repeating unit of a fully substituted cellulose acetate. (Puls, 2011)

The traditional acetylation process (Figure 7) to produce CTA consists of pretreatment with glacial acetic acid and sulfuric acid as a catalyst, followed by the actual acetylation reaction with acetic anhydride and finally the purification of the product by washing with distilled water. CDA can be produced by the acid hydrolysis of CTA. (Ganster, 2013). However, the complexity of the chemical and physical properties of the raw material might cause several complications in the process. (Wilson, 1986)

Usually, the target DoP is around 250-500, depending on the desired end-product. High DoP is equivalent to high viscosity, which may be the target for a certain product or a cause for complications later in process. Low DoP means less bonding and less physical structuring for the fibers, which both attribute to weaker physical properties, e.g. tear strength. Therefore, a satisfactory viscosity level is highly dependent on the application process and raw material of acetylation. However, it is worth noting that DoP should not be the sole property to be analyzed, optimized and targeted, since applications may be connected to reactivity, viscosity, degree of substitution, heat stability and sulphur content as well. (Alén, 2011; Wilson, 1986)

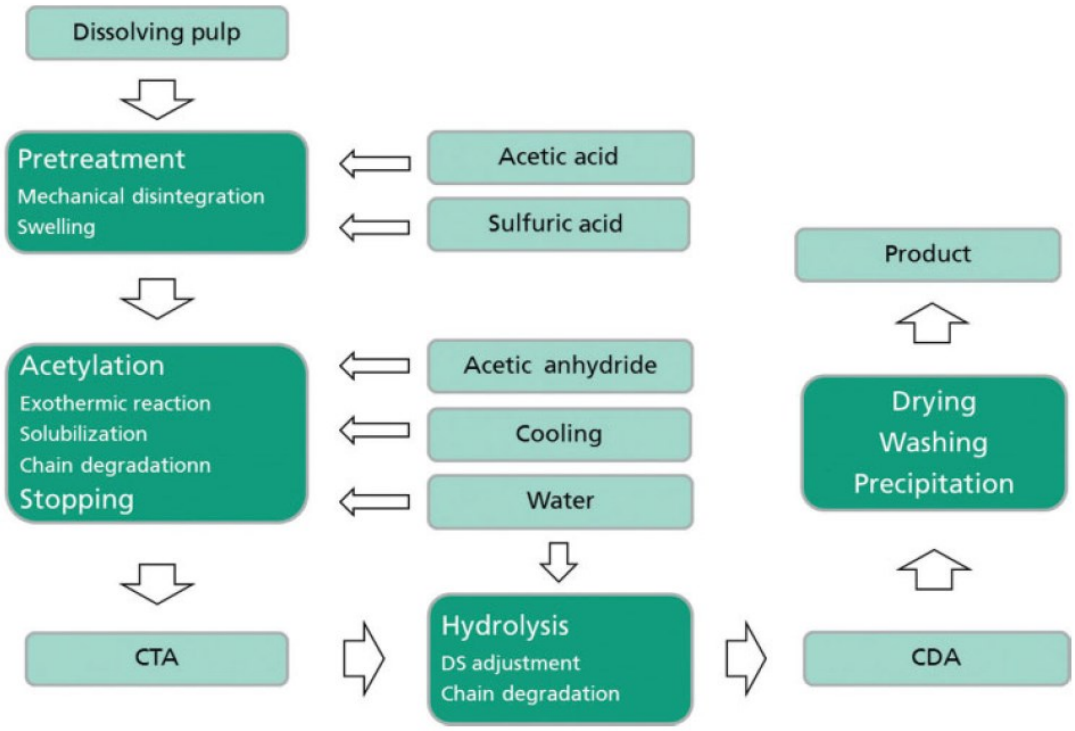

Figure 7. Principle schematic of acetylation process for production of cellulose acetates. (Ganster, 2013)

2.2.1 Commercial-grade cellulose acetate

Several acetate pulps are commercially available with varying properties (Table 2). There is no definitive standard for acetate-grade pulp as they can be produced from several different raw materials with different processes. However, the cellulose purity is the common criterion for the acetate-grade pulp. The cellulose purity requirements for acetate-grade pulp are that the content of impurities should be low, for example hemicellulose content (<1.5 %), kappa number (<0.2) and metal content (<10 ppm) (Saka, 2004; Sato, 2003). Bahia, Buckeye, Solvay Rhodia, Sappi, Borregaard, Rayonier and Weyerhaeuser are the main producers of viscose- and acetate-grade market pulps.

Table 2. Typical properties of market pulp for cellulose acetate production (Adapted from. Saka, 2004)

Producer	Rayonier	Buckeye	Weyerhaeuser
Raw Material	Hardwood mixture	Slash Pine	Western Hemlock and Douglas Fir
Process	PHK	PHK	AS
Xylose (%)	1.3-1.4	1.8	1.7
Mannose (%)	0.8-1.2	1.2	1.5
Alpha cellulose (Wt-%)	97.9-98.4	97.0	95.0
Intrinsic Viscosity (mL/g)	650-750	680	800
Ash (%)	0.05-0.15	0.05	0.12
Fe & Mg content (ppm)	< 3	< 2	< 4
Kappa	0.2	0.2	0.3

2.2.2 Cellulose acetate uses and biodegradability

A significant part of the annual DP production is converted into rayon (cellulose-based textile) products, with lesser amounts to CA. A major part of CA is processed into filter tows. (Thakur, 2017) For the smaller volume applications, CA is used in different products

such as hard plastic products, tool grips, eyeglass frames, biofilm materials, wound dressings, coatings, fire and rot resistant fabrics and even in LCD monitors. (Thakur, 2017; Ihs, 2016; Testova, 2014a; Varshney, 2011; He, 2009; Law, 2004) CA was also proposed as a potential substitute for polypropene yielding higher plastic products. (Budhavaram, 2015)

As the consumers grow more eco-driven, it is good for the companies to be on the winning side and therefore, on the responsibility standpoint. It is therefore important for CA to be regarded as a biodegradable polymer. (Puls, 2011) The degradation pathways are biological degradation and photo degradation. The more widely accepted mechanisms for biological degradation are chemical hydrolysis and dissolution by acetylesterases. Northrop et al. (1987) and Buchanan et al. (1993) reported that in the biodegradation process, deacetylation reactions usually occur first. Biological degradation requires acetyl esterase enzymes, which are present in many microorganisms inhabiting both aerobic and anaerobic conditions. The time or degradation pathways can vary upon microorganism habitats. Light-induced degradation (photo degradation) can also degrade CA, by UV-induced deacetylation. More substituted CA is obviously harder to degrade. For example, CA film with DS 2.5 will take 18 days to degrade in ideal conditions, which is significantly longer than CA film with DS 1.7, which takes only 7 days (Buchanan, 1993; Northrop, 1987). For reference, a regular filter tow with DS of 2.5 takes over a year to degrade in natural conditions. (Puls, 2011; Edgar, 2001)

2.3 Differences in softwoods and hardwoods

Lignocellulosic biomass is a heterogeneous raw material. The natural properties and specifications vary between species, and even between individual plants or trees. Trees can be divided to two major groups: HWs and SWs (Figure 8). (Rowell, 2005) While the cellulose amount remains comparable (Figure 9), the chemical composition and structural anatomy of hemicellulose and lignin differ greatly between these classes and individual species. (Testova, 2014a; Rowell, 2005)

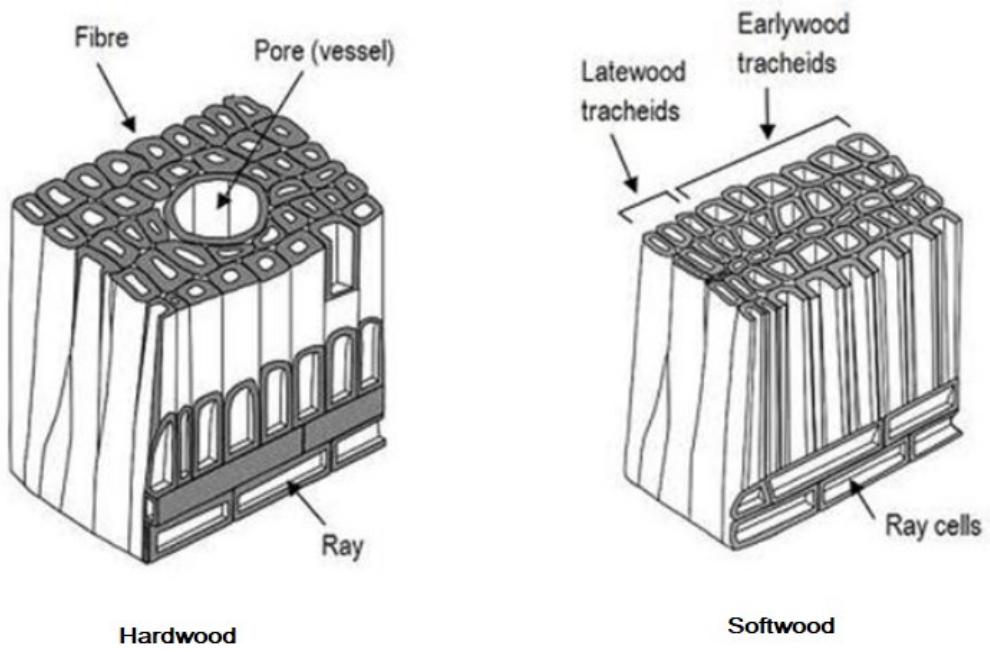

Figure 8. The differences in structures of HWs and SWs. (Adapted from Goto, 2017)

The major structural differences are that HWs have vessels with large cavities, and the storage tissues made of parenchyma cells, which are absent in SW. These pores work as channels to transport nutrients and water through the tree. For SWs, tracheids fulfil this task. Due to this difference, the structure, density and properties of the wood material are different. Additionally, the fiber lengths can significantly differ, since the HWs tend to have shorter fibers (average fiber length 1-3 mm), which cause it to have denser structure (a rough average of multiple species is 750 kg/m^3). SWs tend to have slightly longer fibers (average fiber length 2-4 mm) and so a less dense structure (a rough average of multiple species is 550 kg/m^3). HW structure is also more complex than the SW structure due to these aforementioned reasons. (Rowell, 2005) Naturally, there are exceptions to these claims in species-by-species comparison.

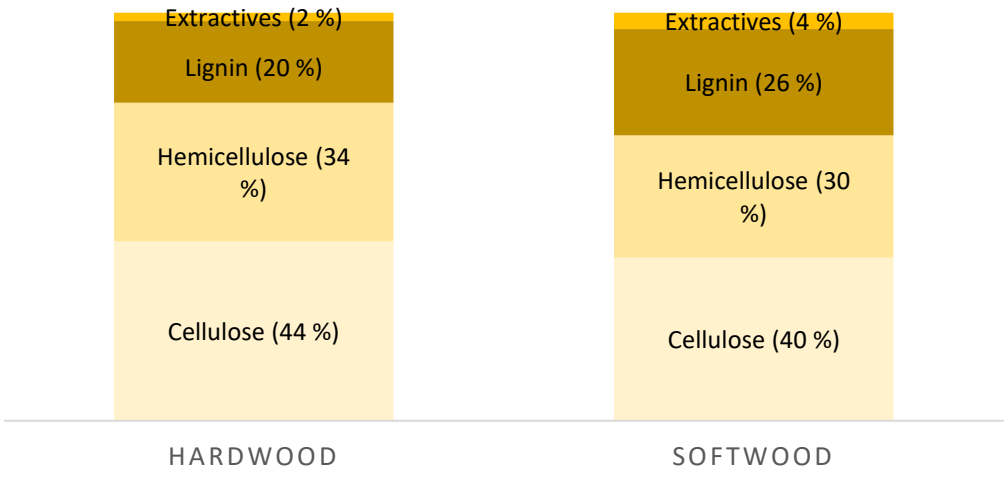

Figure 9. Average composition of HWs and SWs. (Adapted from Sjöström, 1999)

Considering wood's major constituents, hemicellulose, the most significant difference is that in SW galactoglucomannans (15-20 %) are the major part of the hemicelluloses with a minor part being arabinoglucuronoxylan (5-10 %). For HWs, the dominant portion of the hemicellulose is glucuronoxylan (15-30 %) and the minor part is glucomannan (2-5 %). (Sjöström, 1999)

Lignin content also differs between HWs and SWs. The average lignin content is higher in SWs, roughly 25-33 %, with the lignin content of HWs is usually 20-25 %. Chemical composition of lignin differs between the HWs and SWs. The HW lignin is composed of a mixture of copolymer units of coniferyl and sinapyl alcohols in different ratios depending on the wood species, while the SW lignin mainly consists of coniferyl units. Sinapyl alcohol has two methoxyl groups, but coniferyl alcohol has only one. HW lignin contains less free phenolic hydroxyl groups and more benzyl alcohol groups in comparison. (Sjöström, 1999)

In SWs, parenchyma resins are more dominant than the oleoresins and they are distributed more equally in the structure of the wood. HWs also have more parenchyma resins, since they do not have resin canals, in which the oleoresins would be. These parenchyma resins are composed of fats, waxes, triterpenoids and steroids, while the oleoresins are mainly composed of monoterpenoids and diterpenoids, including resin acids. (Sjöström, 1999)

All these factors affect the processability, usage and properties of the wood raw material, and the nature of the raw materials should be considered for process optimization.

3 Cellulose acetate process

The aim of the CA process is to produce the CTA dope, which can be, for example, spun, molded, extruded or cast into films. Acetate-grade pulp is required for successful acetylation. CTA can be further refined to CDA or CMA. (Wilson, 1986) One process step towards acetate-grade pulp is the purification with CCE and bleaching. Acetylation starts with an acidic pretreatment to activate the acetic acid anhydride by electrophile formation. The activated pulp then undergoes an acetylation step by acetic anhydrides to form CA. The formed CA is washed and dried and is now ready for the applications. The acetylation reaction results in primary CA, i.e. CTA, which can be further treated by alcoholysis or hydrolysis, with e.g. methanol or water, to CDA or CMA. After the desired acetylation reaction is completed, acids, unreacted pulp and cellulose acetate need to be separated in a washing step to obtain the target product. (Iketomo, 1980; Yabune, 1983) Naturally, CA processes can be the variations of these four primary steps. In general, acetylation is performed in three to four steps: pretreatment, acetylation, refining and purification.

The main product is cellulose-2.5 acetate (CDA), which is converted to fibers by a dry-spinning process. First, dope with 15-40 % concentration is formed by dissolving CDA with acetone. Then, the dope is filtered, de-aired and pre-heated so it can be extruded through a spinneret while hot air (100-250 °C) is evaporating the acetone and solid filaments are forming. The filaments are drawn and stretched by godets to align its molecules and to enhance strength of the filament, while it is still plastic from the heat. The filaments are combined by twisting into a yarn and wound onto a package by ring and traveler system. Typical spinning velocities for cellulose acetate range from 200-400 m/min and the solvent is recovered in the process with activated carbon and distillation. (Imura, 2014)

3.1 Cold caustic extraction

Cold caustic extraction (CCE) in pulping processes is usually performed after the cooking stage for further hemicellulose removal to produce acetate-grade pulp. For a successful CCE treatment, the preceding process steps should be incorporated with removal of hemicellulose, e.g. in PHK, the prehydrolysis or in AS, the hot caustic extraction, to preserve reactivity. (Sixta, 2006) CCE process is efficient at removing hemicellulose in mild conditions with minimal impact on the lignin and cellulose fraction. However, due to the non-selective nature of the alkaline treatment, some interactions and reactions occur with extractives and lignin while hemicelluloses undergo numerous reactions (Figure 10). (Testova, 2014a) The main parameters in CCE process are time, temperature, pressure, the concentration of alkali and the alkali charge. The CCE process, as the name suggests, is performed in low temperatures, but also at high consistency to avoid dilution of the NaOH and to decrease the amount of spent effluent in the recovery. In optimal conditions, the fibers swell, and the hemicelluloses are dissolved to the reaction medium. (Ragnar, 2013)

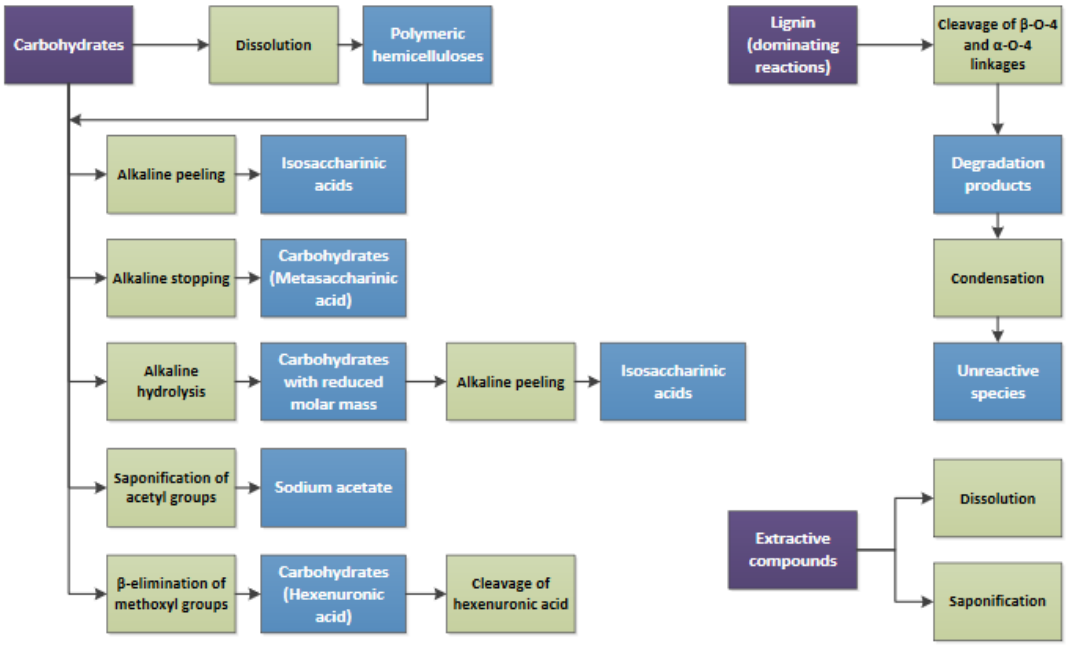

Figure 10. Simplified scheme of alkaline pre-extractions (CCE) interactions on different components of wood. (Testova, 2014a)

NaOH concentration is the main factor affecting the xylan removal; the higher the NaOH concentration, the higher the xylan removal. However, the xylan removal stagnates at the residual content of 0.7 %, after which xylan has been observed to be alkali resistant. Such low xylan content can only be obtained at the expense of cellulose yield, viscosity and overall quality of the pulp. The optimal NaOH concentration is usually 100 g/L (Figure 11), where >1.5 % hemicellulose content is expected if other process steps are performing well. High consistency of over 35 % is recommended to avoid dilution of the caustic mixture, however modern applications work in medium consistency as well. An increase in time does not significantly affect the maximum xylan removal, while higher temperature reduces CCE efficiency. In summary, xylan removal is the most efficient at lower temperatures in an optimal amount of chemicals. (Sixta, 2006)

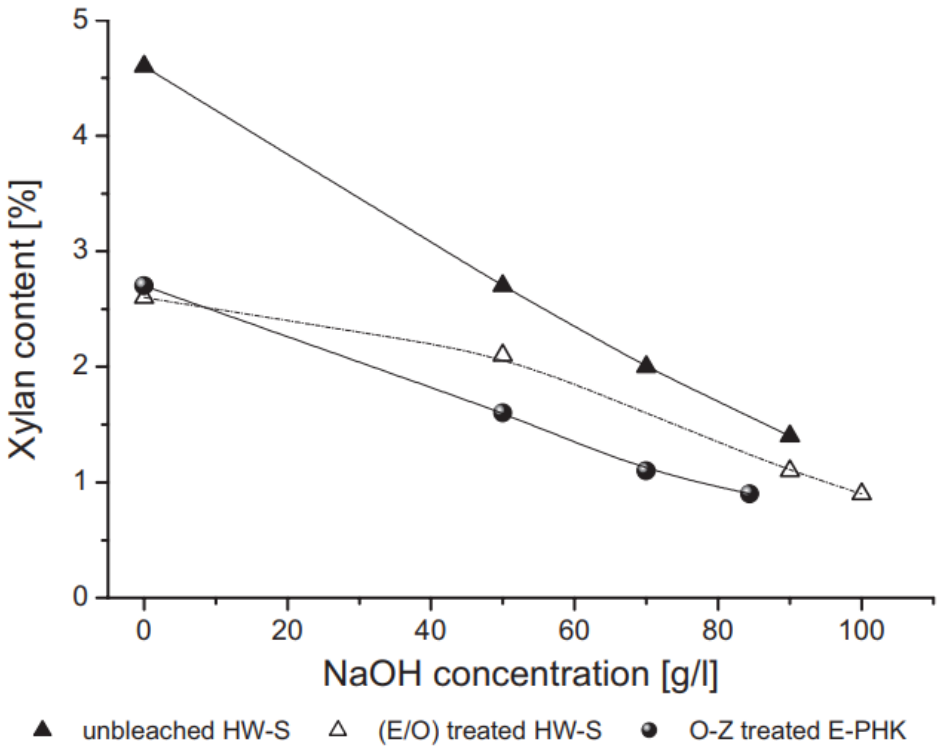

Figure 11. Relation between xylan removal and NaOH concentration. (Sixta, 2006)

NaOH's dissolution potential is limited to low DoP carbohydrate fragments, while the higher DoP cellulose fractions remain mostly intact. This allows the removal of low DoP fragments and alkali-soluble impurities. Cellulose yield losses are approximately 1-1.5 %

for each percentage gain in α-cellulose content. Even with the aforementioned losses, CCE is still considered as the most selective and the most effective way to remove xylan from HW pulps. Hemicellulose removal is vital since xylan precipitates easily on fiber surfaces, impairing the pulp reactivity and accessibility. CCE is less effective for SW pulps, due to the presence of the alkali resistant mannan. Concentrations of alkali higher than 11 % can induce the alkali cellulose formation, which regenerates to cellulose II during washing, forming extra hydrogen bonding, resulting in undesirable decrease in reactivity of the pulp. (Roselli, 2014; Sixta, 2006; Rydholm, 1966) The efficiency of CCE can be measured with R_{18} and R_{10} values in addition to residual hemicellulose content. (Sixta, 2006)

In industrial applications CCE (Table 3) should be combined with an alkali process such as pre-hydrolysis kraft cooking (PHK). Alkali extracts impurities from the pulp and is slowly contaminated, therefore the recycling of the lye can be challenging. The recycled lye should not be used in the CCE of the subsequent cook, but rather in the cooking step where the effect of the impurities on the reaction is minimal. Ideally, fresh lye should be used in CCE and recycled to the cooking step. Besides, most of the impurities will be purified in the cooking step, as the impurities are transferred away from the process with the cooking liquor, primarily the black liquor. (Sixta, 2006)

Table 3. Typical values for CCE stage in DP production. (Ragnar, 2013)

Retention time	10-20 minutes
Inlet temperature	30-40 °C
Pressure at the top	Atmospheric
Alkali charge	50-120 kg/BDt (Eq. 5-12 %)

Modern applications of DP require high reactivity. Pulp reactivity increases due to the removal of hemicellulose and low molecular weight cellulose, but is also hindered due to the fibril aggregation or the alkali-induced transformation from cellulose I to cellulose II (increased hydrogen bonding). The formation of cellulose II can be minimized by careful selection of reaction conditions. Increasing the NaOH concentration in CCE is reported to lower the reactivity of the DP raw material. Additionally, post-CCE-treatment such as mechanical refining, steam explosion and sulfuric acid hydrolysis are not advisable, since

these post-treatments lower pulp DoP and reactivity, which is not beneficial for the acetylation process. (Dou, 2017)

3.1.1 After-CCE-Washing

Washing is performed after the CCE extraction. Washing aims to reduce the amount of impurities and reaction chemicals from the pulp after the reaction while the pulp is homogenized. Industrial pulp washing in pulp mill are performed with different washers, e.g. press washing equipment, vacuum drum washer or displacement washer. While the machinery is different, the methods have common principle of washing, which consists of four processes: dilution, dewatering, diffusion and displacement. Multistage washing with counter-current principle is the industry standard for optimal pulp washing, while hornification is minimized. (Santos, 2014)

3.1.2 Effect of concentration, time and temperature on the CCE process

Xylan and cellulose structures undergo peeling reactions during the alkaline conditions of the CCE, which cause the xylan backbone to degrade. The reaction that counters this degradation is the stopping reaction, which stabilizes the structure and halts the degradation. At lower temperatures, the peeling reaction occurs at a higher rate to xylan than to cellulose structures. In higher temperatures, the peeling reaction rate increases for both cellulose and hemicellulose, so the reaction is less selective towards hemicellulose. Lower temperatures also increase the removal of xylan from the pulp and the amount of dissolved hemicellulose as seen from Figure 12. Increasing the NaOH concentration past 100 g/L in fact weakens the effect of xylan dissolution in lower temperature. Increasing the temperature generally increases the NaOH consumption. (Sixta, 2006)

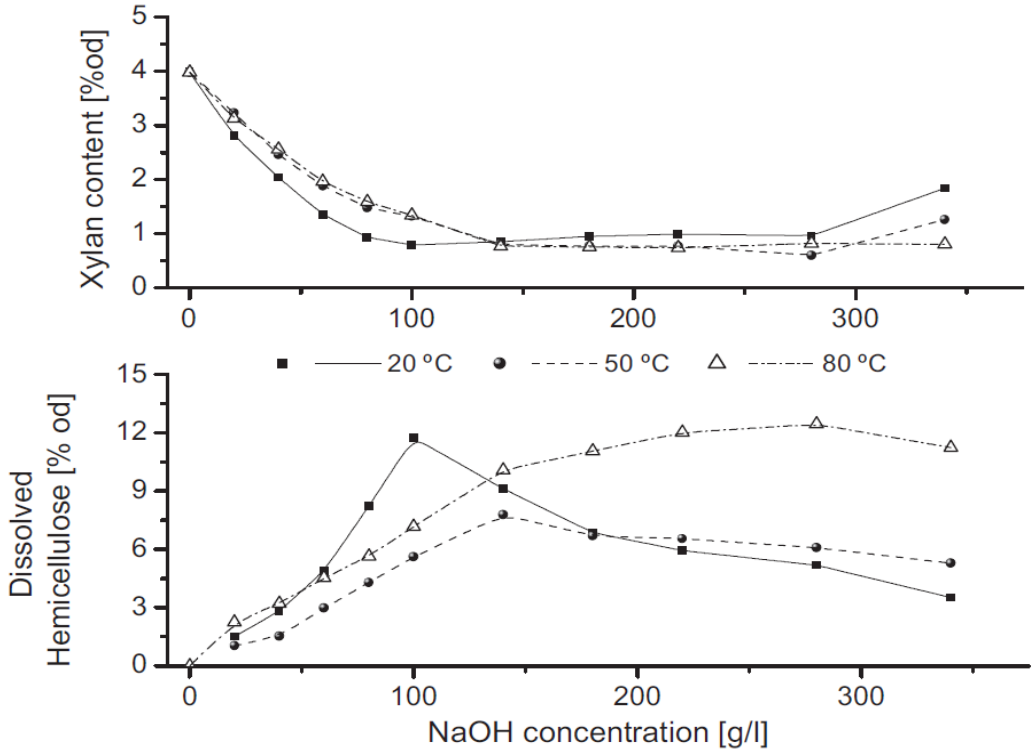

Figure 12. Xylan content in increasing NaOH concentration (upper) and the amount of dissolved hemicellulose (lower) at different temperatures. (Sixta, 2006)

Swelling and side reactions occur relatively rapidly during CCE, therefore prolonging the CCE does not further reduce the xylan content (Figure 13). Theoretical optimum temperature for CCE in laboratory is 20 °C. In a pulp mill, the temperature is generally higher due to equipment or process restrictions. Therefore, an increase in alkali concentration is required for a similar xylan removal rate. For comparison, increasing temperature from 30 °C to 50 °C results in xylan removal decrease of around 27 %. However, some pulp mills operate at compromise temperature of 35 °C, in which the xylan removal, alkali charge and cooling costs are reasonable. (Sixta, 2006)

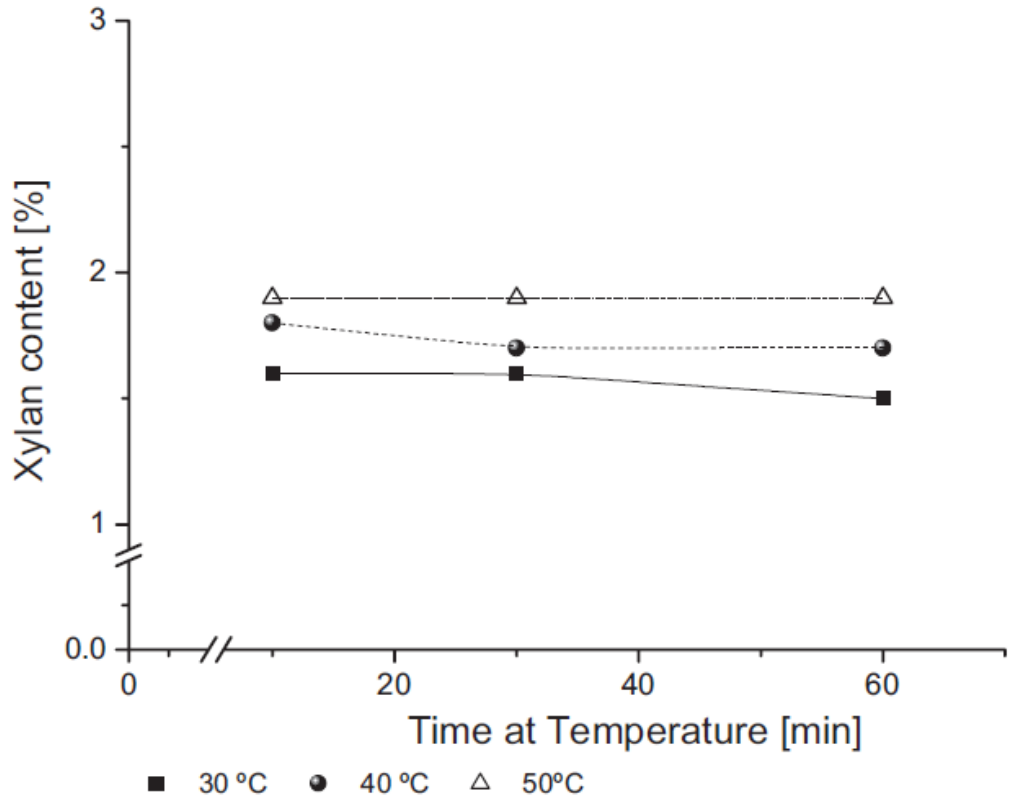

Figure 13. Effect of time to xylan removal during CCE. (Sixta, 2006)

3.2 Elemental Chlorine Free (ECF) Bleaching

ECF bleaching processes are generally chlorine dioxide (ClO_2) based. ClO_2 has the excellent bleaching properties of chlorine, while being in a more manageable and environmentally safe form. ECF bleached pulps generally have higher DoP and higher brightness and brightness stability due to the lower free phenol group content in lignin and carbonyl group content than the Cl bleached pulps. (Perrin, 2017) ClO_2 is a chemically more stable compound, causing less radical formation and quality variation in localized areas, which results in constant quality of bleached pulp. ECF sequences allow higher reaction temperatures, resulting in faster reactions and increased production capacity. (Virkkola, 1983)

PHK processes yield high purity level pulps, requiring less intense bleaching processes since the lignin and hemicellulose contents are significantly lower than, for instance kraft pulp. (Mahlamäki, 2015) The specifications of DP bleaching sequence depend on the cooking process and raw material. As different mills have different equipment, from

modern to relatively obsolete, the operational conditions can still vary greatly. Good operational execution and viscosity control in cooking and bleaching are still required to achieve the desired product properties. (Sixta, 2006; Siltanen, 1968)

Washing is conducted between bleaching stages to remove residual compounds as shown in Table 4. These compounds range from impurities to residual chemicals and can cause unwanted side reactions. The washing technique is generally counter-current washing by water. In pulp mills, river water is often used and therefore washing water itself can have some residuals from outside of the process. Impurities in pulp and water are mainly transition metals such as manganese, copper and iron. In laboratory, the washing stage can be performed in several different ways, usually carried out with de-ionized or distilled water. (Sillanpää, 2005; Orko, 2000)

Table 4. The removal target of washing (Modified from Sillanpää, 2005)

Stage	Primary targets	Secondary targets
Before O_2 delignification	Organics	Transition metals (Mn, Cu, Fe)
Before bleaching	Organics	Base components
D_0	Sodium Organics Ca, Si, Mn	Acids
EOP	Organics	Pitch, residuals
D_1	Acids	Organics, residuals
E_2	Alkalinity	
D_2	Chlorides	
P	Transition metals	Residual chemicals

3.3 SO_2 wash

Sulfur dioxide water (SO_2) washing is performed after brightening stage in ECF sequences to inhibit any side-reactions and to terminate the remaining reaction chemicals. Elimination of residual chemicals stabilizes the pulp and improves the longevity of the pulp. SO_2 washing method after the P-stage reduces the amount of residual peroxide and

removes acid soluble metal salts. SO_2 also degrades the remaining lignin trace in several reaction pathways. (Sixta, 2006)

3.4 Different cellulose acetate novel processes

Acetate-grade pulp is produced with several different processes, with AS process and PHK process being the most prevalent in DP production. (Sixta, 2004) However, the process conditions vary between mills due to raw materials and execution.

AS pulping process produces high-quality DP with efficient side-stream management. Hemicelluloses and lignin are recovered in large quantities for additional revenue. (Sixta, 2013) However, AS pulping process is unsuitable for several wood species, such as oak and gum wood, which causes restrictions in usage of this method. (Saka, 2004)

Yuan et. al (2017) produced high-quality acetate-grade DP from low-quality bamboo DP using alkaline pre-extraction (similar to hot caustic extraction in this case), kraft pulping, xylanase treatment, CCE (6 % NaOH) and ECF bleaching, yielding a pulp with *ca.* 97% α-cellulose and under 2 % hemicellulose with 0.08 % ash. Side streams of the process are ethanol, lignin and silicon. The process takes significantly longer than the traditional CCE processes to ensure the removal of xylan. The study shows good trends on pulp quality with practical maximum values in laboratory conditions.

Borrega et al. (2013) also produced HW DP from birch using hot water extraction combined with S-AQ process resulting in 3-5 % xylan content pulp with high yield. However, in their experiments, if the xylan content was below 3 %, the yield decreased rapidly.

He et al. (2007) produced high-grade CA from PHK bamboo pulp with xylanase enzyme, potassium peroxymonosulfate (oxone) and ECF bleaching. Pulp had high crystallinity and yield, while being similar to traditional acetate pulps. Xylan content was 3.9 %, 88.4 % ISO brightness and ash of 0.1 %. Their method focused on having high crystallinity over any other parameter, which might be necessary for some pulp applications. However, reaching low to medium grade CA from cheaper raw material shows potential.

Roselli et. al (2014) reported that an ionic liquid treatment (IONCELL-P) for paper-grade kraft pulp results in high-quality DP suitable for e.g. CA production. Additional

endoxylanase treatment was performed and the resulting pulp had 1.7 wt-% hemicellulose content. Hemicelluloses and lignin were extracted in pure fractions and valorized in this method. (Roselli, 2014)

4 Analysis of pulps

The pulps were characterized with international standards and established protocols in the laboratories of the Department of Bioproducts and Biosystems. This chapter gives an overview of the roles of the analyses, and their information value on the overall pulp quality.

4.1 Lignin content

The lignin (and hexuronic acid) content of pulp is expressed as kappa number, which can be measured in real time in the process or by chemical analysis in laboratory. Lignin content can also be estimated with H-factor in kraft pulping processes. The lignin content consists of acid-soluble lignin and Klason lignin, which can be calculated with kappa number with different factors. The amount of bleaching chemicals required to reach certain brightness level of pulp can be approximated from the kappa number. (Iakovlev, 2011; Fardim, 2011; Sixta, 2006)

Klason and acid soluble lignin are determined by NREL/TP-510-42618 standard while kappa number is measured by ISO 302:2004 and T 236 om-99. (ISO, 2004; Tappi, 1999).

4.2 ISO Brightness

Brightness is one of the most important properties of the pulp products as it relates to the impression of quality and it is the first attribute to be examined.

Brightness is defined as reflectance of visible blue light and it is measured optically from the surface of the naturally colored pulp sheets (i.e. no additives) by detecting the reflected light at 457 nm effective wavelength. In pulp analyses, normal brightness ranges between 20 % ISO brightness of unbleached kraft pulp and 95 % ISO brightness of 95 % of

fully bleached DP. (Sixta, 2006) Industrially produced high-end pulp sheet generally have 90.5-92 % ISO brightness.

Brightness, a signal of a successful bleaching, is affected by chromophore content from lignin. Brightness indicates the removal of lignin-based coloring compounds in, for example cooking or pretreatment. (Dence, 1996) The method is presented in standards ISO standard (ISO 2469, ISO 2470) or TAPPI standard method (TAPPI T 452). Brightness analysis method was performed according to the ISO standard (ISO 2470-1:2016) in this thesis.

4.3 Carbohydrate analysis

The carbohydrates analysis estimates the internal carbohydrate composition relation and lignin content of the pulp. Mannose and xylose contents represent the hemicellulose content in wood DPs. In the acetate pulp analyses regarding cellulose pulp purification, the xylan and (galacto)glucomannan contents are the most relevant since the remaining glucomannan can react to glucomannan acetate, which has been associated with poor filterability and abnormal viscosity. Xylan can react to xylan acetate, which contributes to coloring, poor filterability and hazing in the process. (Saka, 2004; Sjöström, 1999; Wayman, 1958)

Sugar analysis was performed according to NREL standard (NREL/TP-510-42618).

4.4 Acetone extractives

Acetone extraction is used to extract wide array of woods extractives. The amount of acetone extractives measure wood's acetone-extractive constituents and non-structural components. Usually, only acetone soluble extractives are measured to estimate extractive content of a pulp sample. (Sjöström, 1999) The standardized method uses a Soxhlet extraction reflux system with controlled temperature and reflux rate. After a certain amount of refluxing, the acetone is gathered and evaporated to determine the acetone extractives content. Acetone extraction was performed according to standard SCAN-CM 49:03.

4.5 Ash Content

For pulpwoods, the content of inorganic components is usually between 0.3 % to 1 % of the dry solids, depending on the species and the environment in which the tree grew. (Sjöström, 1999) The ash consists of mineral salts, metals and oxides after incineration of the sample. Kraft pulp contains Na, Fe, Mn, Cu and other trace elements, which are present in most of the pulps. (Sixta, 2006) Ash content was measured according to the ISO1762:2015. In short, pulp samples are incinerated at temperature of 525 °C and the resulting amount of ash is measured gravimetrically.

4.6 Total Organic Carbon, TOC

TOC indicates the total amount of organic carbon present in the water solution including carbon dioxide and carbonate ions. The organic carbon from the solution is oxidized to carbon dioxide with an oxidizing agent or highly energetic radiation, for example with UV. The formed carbon dioxide is measured and analyzed with several techniques, such as infrared spectrometry, titration or conductometry. A common way of conducting the TOC analysis for pulp is to dilute the sample, acidify it, lead the sample with eluent to an oven to be gasified in high temperature (e.g. T=680 °C) and analyze the gas with non-dispersive infrared detector (NDIR). (Lut, 2017; Shankar, 2013)

4.7 R_{10}, R_{18}, S_{10}, S_{18}

$R_{10,}$ R_{18}, S_{10} and S_{18} values indicate the degree of solubility of the pulp in sodium hydroxide (NaOH) solution of 10 % or 18 %. The test is standardized to certain specific conditions (Tappi T 235), which indicates the level of cellulose purity. Residual portion of the cellulose is given as R_{10} or R_{18} as a percentage, while the soluble portion of the cellulose in the test conditions is referred as S_{10} and S_{18}. The test is based on the knowledge of 10 % NaOH solution being able to dissolve the low DoP cellulose and hemicelluloses present in the pulp, whereas the 18 % NaOH solution can dissolve most of the hemicelluloses, leaving the cellulose dissolution to a minimum. These tests can be used to indicate that subtracting S_{10} from S_{18} is roughly the amount of degraded cellulose, and R_{10} indicates the high molecular weight (Mw) cellulose content. These values can be determined

gravimetrically from the residual pulp or by titration of the residual solution. (Saka, 2004; Tappi, 2003)

4.8 Gel permeation chromatography, GPC

GPC determines several structural characteristics from pulp, for example number-average molecular weight from a sample with particles of different length and size. (Sixta, 2006) GPC analysis consists of solvent exchange, dissolution and the actual measurement. After the pretreatment, the samples are analyzed with high-performance liquid chromatography (HPLC). HPLC utilizes a solid stationary phase and a liquid moving phase to separate compounds according to their Mw. The separated compounds are analyzed with a detector to quantitate different amounts of molecular weight compounds. (Penttilä, 2013) Viscosity, polydispersity index (PDI), molecular weight distribution and several other structural properties of the pulp can be calculated from the GPC data. The calculated viscosity reasonably matches the pulp intrinsic viscosity (<10 % difference) or it may vary significantly (>30 % difference), depending on the sample data. (Maccreath, 2012; Ouano, 1973) The most important calculated values are number average molecular weight average (Mn), weight average Mw, Z average molecular weight (Mz) and polydispersity index based or Mw/Mn (Figure 14). (Maccreath, 2012)

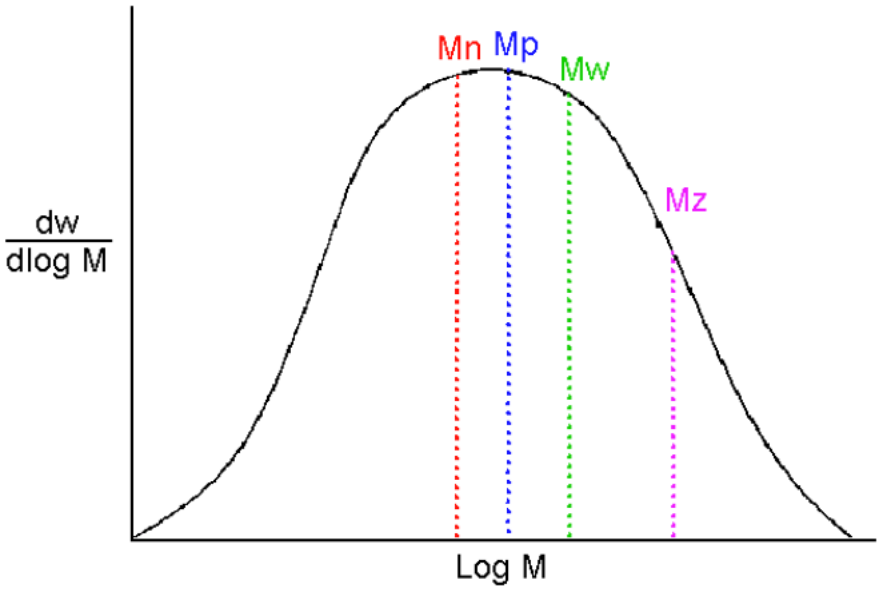

Figure 14. Different statistics that can be analyzed from the GPC data. (Maccreath, 2012)

GPC was performed according to internal protocol of the Department of Bioproducts and Biosystems. The method includes solvent exchange in water, acetone, and DMAc, followed by dissolution in LiCl-DMAc. The analysis was performed with a Dionex UltiMate HPLC 3000 SEC.

4.9 Intrinsic Viscosity

Intrinsic viscosity indicates the average molecular weight of the polysaccharide fraction. The unit is milliliters per gram [mL/g] and the values indicate average DoP. Intrinsic viscosity with other parameters indicates e.g. selectivity of CCE process and paper-grade pulp strength. Conventional viscosity values for PHK DP are around 400-700 mL/g. In pulping and bleaching, cellulose degradation is estimated by intrinsic viscosity. (Sixta, 2006)

Viscosity and rheological properties are tightly intertwined as the viscosity affects, for example heat transfer and the pumpability. Viscosity is defined as the ratio of shear stress to the shear rate of fluid under shear force. (Sjöström, 1999) Intrinsic viscosity is defined as the reduced specific viscosity in the limit of “infinite dilution”. (Harding, 2013) The viscosity indicates the molecular weight fraction distribution. The molecular weight fraction distribution can change due to removal of smaller weight fraction compounds, such as hemicelluloses in pulp processes or due to degradation of higher weight fraction compounds, such as cellulose chains. (Sixta, 2006)

Viscosity was measured according to the SCAN-CM 15:99.

4.10 Metals analysis from pulp

A traditional pulp sample contains metal ions, such as Mn, Cu, Fe, Mg, Al and traces of several others. The metals can interfere with chemicals or catalyze reactions to degrade chemicals or pulp. The metal content in pulp itself is usually low, but metals can accumulate in the process over time, e.g. in the washing system with recycled water flow. Other sources of metal ions can be impurities in the raw material feed, corrosion of equipment or accidental addition of material. Typical metal contents vary between 0-20 ppm for CA pulp and 0-50 ppm for viscose grade pulp. (Sixta, 2006; Sjöström, 1999) Metal content of pulp can be analyzed with, for example atomic absorption spectrophotometer

(AAS) from ashed pulp sample with hydrochloric acid dissolution. The metal analysis can be performed according to TAPPI T 266 om-02.

4.11 CCE pulp and residual analysis

After the reaction, the following analyses were performed to evaluate the efficiency of CCE treatment: brightness, viscosity, kappa number, GPC, carbohydrate composition, lignin composition, total organic carbon (TOC) and yield.

4.12 Triacetate analysis

American Society for Testing and Materials (ASTM) has listed a standard set of CA analyses in Designation: D 871-96 (reapproved 2004). The following tests extensively characterize the CA: moisture content, ash content, free acidity, combined acetyl or acetic acid content, hydroxyl content, primary hydroxyl content, sulfur or sulfate content, heat stability, intrinsic viscosity, viscosity, color and haze. (ASTM, 2004)

Standard analyses for CA analyses are at least ball drop viscosity, haze (turbidity) and ultraviolet-visible light spectroscopy (UV-Vis) to measure yellowness. The calculation method for the yellowness is presented in the chapter materials and methods. Additionally, combined acetyl and acetic acid content (degree of substitution) can be measured. After the basic analyses, one can further analyze other relevant properties that can vary.

5 Cellulose acetate market and future prospects

The production of DP will likely increase in near future after remaining fairly stagnant, (Figure 15) due to the increase in demand of textile products and specialized applications in e.g. construction and tools. The increase in DP availability will reduce the price, but also present possibilities for new CA products as well. In the further future, the increasing knowledge of cellulose-based products will continue to increase the variety of products available in the market and research. With today's knowledge, CA products will likely be an intermediate technology in the cellulose revolution, but another technology will

prevail and conquer the market. This is due to the restrictions in the CA process, the product quality, competing technologies, high prices related to competing products and tightening environmental legislation. However, the current technologies are constantly improving and several new or established methods for CA production have been introduced or improved, for example Batalha (2012), Roselli (2014) and Yuan (2017). CA is considered as specialized raw material for niche applications rather than bulk raw material in today's market. However, the research is still going strong and one could even say that recent years might have be the golden age of CA research.

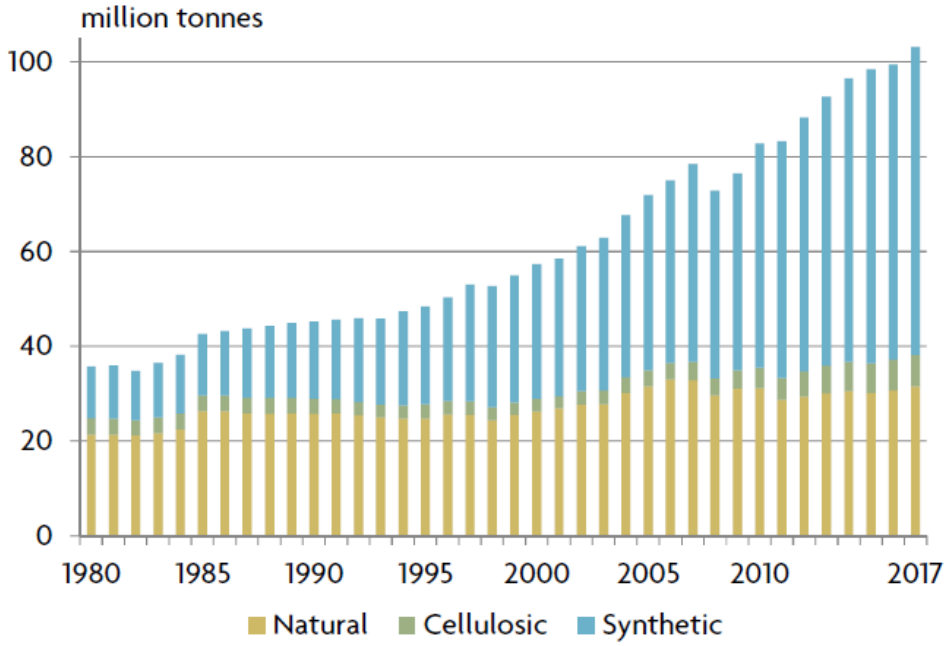

Figure 15. World fiber consumption ranging from 1980 to 2017. (The Fiber year, 2018)

Market for CA has been predicted to increase from US $3.61 B in 2016 to US $4.87 B by 2022. The drivers for growth are the increased consumption of textiles, non-flammable materials for specialized applications, plastics and other existing products. The greatest increase in commerce is estimated to come from Asia Pacific (APAC) region (Figure 16). (Market Research Report, 2018) In retrospect, the market size in 2005 was nearly US $3 B, with cigarette tow market share being about US $2.45 B. (Serad, 2009) The size of the market has been comparatively low, and the average annual market growth has been about 1.1 % in the period 2005-2016. The predicted annual market growth for CA is 4.3-

4.4 % from 2016 to 2022 due to demand increase in developing markets (Figure 17). Traditionally, United States, Western Europe and Asia are the main consumers of CA textiles. (Law, 2004)

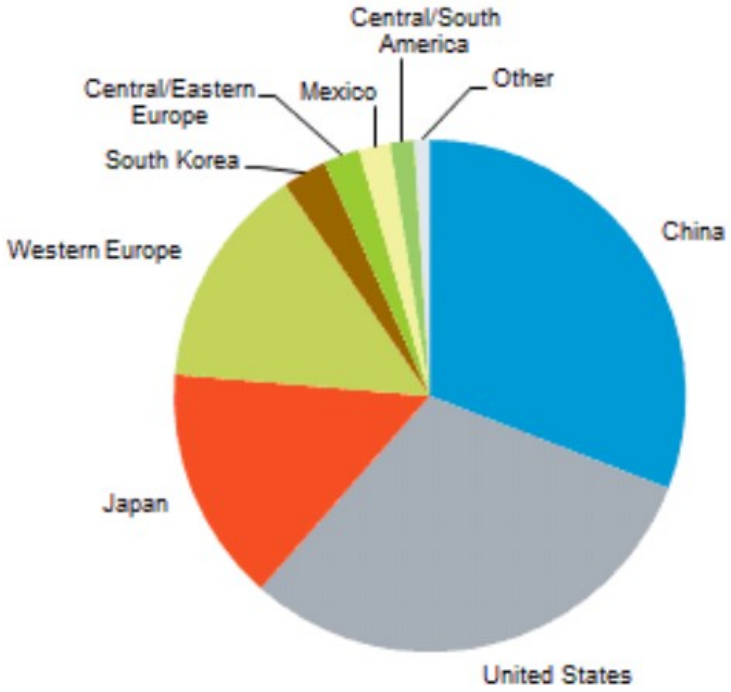

Figure 16. Cellulose acetate flake consumption by countries. (IHS, 2016)

Manmade fibers (MMF) are chemically made fibers. The MMF market has been growing on average of 4.4 % annually since 1980 (14.3 Mtons) to 2017 (71.6 Mtons). The driving force in production and consumption was population growth, especially with China as the main producer and exporter of textiles. Currently, CA has two major commercial usages; in textiles or textile blends and in CA tow used in e.g. cigarette filters. CA tow consumption in cigarette filter industry has decreased in recent years and is expected to further decrease in the future with declining cigarette consumption. However, in the textile applications, the demand has increased steadily. (The Fiber Year, 2018)

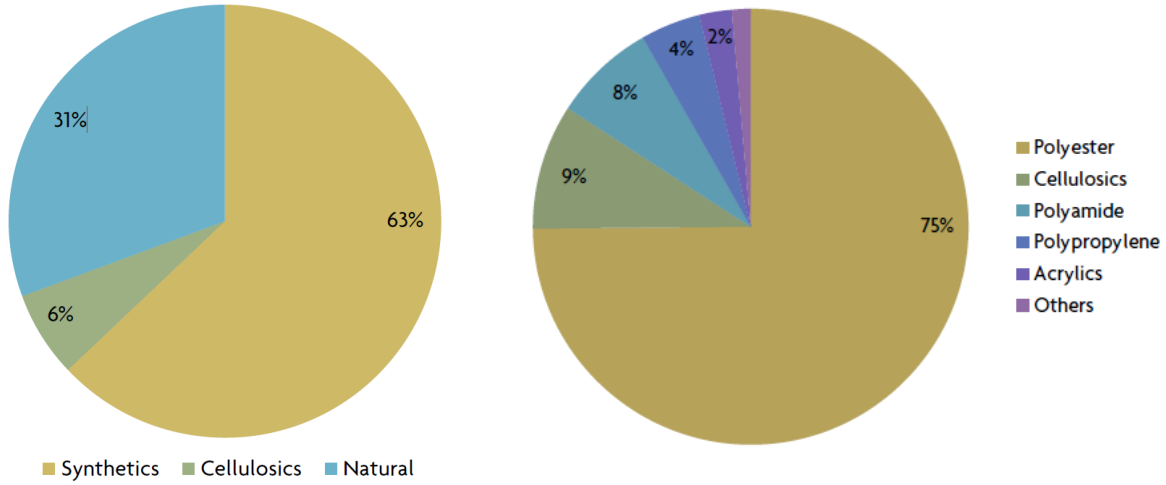

Figure 17. World Fiber Market in 2017 (left) and the MMF market in 2017 (right). (The Fiber Year, 2018)

MMFs market has been growing faster than the market of natural fibers. In the MMF section, cellulosics share growth is outpacing the polyester production increase, which has been dominant in the category of MMF growth. However, the growth of cellulosics has also been relatively slow in recent years. Figure 18 shows relatively stable decline and stabilization of the observed CA production.

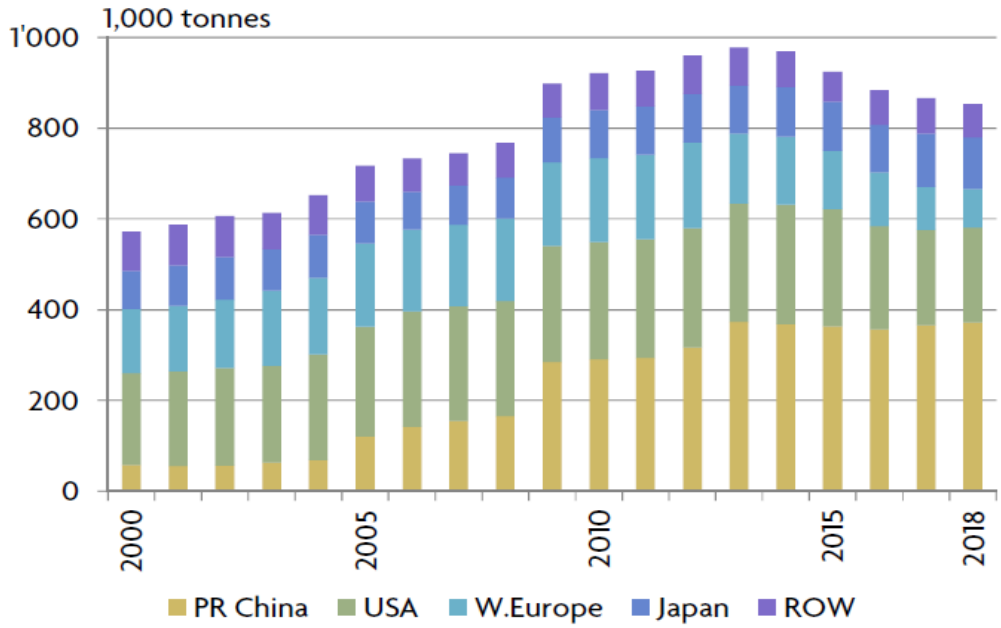

Figure 18. Cellulose acetate filter tow production by producing countries. (The Fiber Year, 2018)

In the future, CA products such as textile, medical, agricultural, pest control, optical and composite applications can be expected. The new products will likely remain in fairly niche markets and the availability of CA could decrease the price. Gradual increase in availability would be healthy for the research and markets, since the availability would not be the bottleneck due to pricing. Currently, the market is in a good place regarding price and availability for the producers. However, the high price hinders some of the more bulk applications from reaching the broader market.

Near future examples of the CA applications are high value medicinal applications, such as controlled release –products, in which a medicinal substance with particular properties is contained in a CA shell, which degrades in certain conditions, for example after a certain amount of time or in certain pH. Following the degradation, the substance will be released from the shell and apply its benefits around it. Other commodity applications include additives in fillers, binders, membranes, new polymer materials, construction materials, new laminate methods and fire-resistant textiles. (Qiu, 2013; Edgar, 2001)

EXPERIMENTAL PART

6 Materials and methods

6.1 Laboratory plan

The main objective of the laboratory experimentation is to establish a working test process and analysis setup to conduct research on cellulose acetate production from lower-grade dissolving pulp. Once the process conditions and methods of analysis are established, the quality and repeatability are tested. After the verification of process' operability, the process can be optimized to produce CA with suitable properties. The same process is then performed for various pulps from different sources. These pulps represent hardwood dissolving pulps (HWDP), softwood dissolving pulps (SWDP), hardwood brown stock (HWBS) and commercial DPs (e.g. mixture of HW/SW or various HWs or SWs).

6.2 Materials

The experiments were conducted with the laboratory equipment, reagents, materials in the facilities of Aalto University's Department of Bioproducts and Biosystems. The reagents and chemicals are commercially available products. The most notable chemicals used in this study are acetic acid, acetic anhydride, sulfuric acid and sodium hydroxide.

Different DP samples were obtained from Enocell mill. Analysis of commercial acetate-grade pulps were included for comparison. DPs were characterized, and results are presented in following chapters. Metal content of the pulps were analyzed in Research Center Imatra (RCI) laboratories.

HWBS, bleached softwood dissolving pulp (SWBL) and bleached hardwood dissolving pulp (HWBL) analysis results are presented in Table 5 below. HWBS was obtained from Fiberline 1 of Enocell mill. The fiberline consists of pretreatment, cooking, O_2-delignification, bleaching, washing and storage. The HWBS was sampled after oxygen delignification, and before the bleaching process. Commercial pulp samples were obtained from the free pulp market for reference purposes. A wider range the carbohydrates were analyzed, but the most relevant values are presented. The HWBS pulp has slightly higher xylan content than the HWBL, corresponds to the xylan reduction

during bleaching. The SWBL has naturally a lower xylan content, but higher glucomannan content.

Table 5. Dissolving pulp raw material properties.

Characteristics	HWBS	SWBL	HWBL
ISO brightness [%]	55.4 ± 0.6	89.3 ± 0.2	90.8 ± 0.3
Viscosity [mL/g]	632 ± 9	392 ± 4	475 ± 12
Kappa number	3.3 ± 0.5	0.3 ± 0.1	0.5 ± 0.1
Ash [%]	0.6	0.4	0.2
Acetone extractives [%]	0.67	0.09	0.12
Cellulose [% on pulp]	92.7	93.2	92.8
Xylan [% on pulp]	6.9	3.6	6.7
Glucomannan [% on pulp]	0.4	3.0	0.4

6.3 Initial preparations

Brown-stock industrial pulp samples were washed with an excess of ion-exchanged water to eliminate residual chemicals and other impurities. Excess water was removed by a centrifugation and the samples were stored in cold storage in closed plastic bags.

6.4 Dissolving pulp CCE

Pulp samples were analyzed in set conditions – constant mixing with two different temperatures, constant time, and six different NaOH concentrations as presented in Table 6. The major difference between the mill setup and the experimental setup was that the consistency is significantly lower. In the pulp mill, the consistency is ranging from medium (10-18 %) to high (30-35 %) consistency. This change was due to the limitation in mixing of laboratory equipment, therefore lower consistency was required to ensure even distribution of the chemicals.

Table 6. CCE parameters of the different test series.

Test run	Time [min]	Consistency [%]	Concentration [g NaOH / L solution]	Temperature [°C]
1 / 7	30	5	50	30 / 60
2 / 8	30	5	60	30 / 60
3 / 9	30	5	70	30 / 60
4 / 10	30	5	80	30 / 60
5 / 11	30	5	100	30 / 60
6 / 12	30	5	120	30 / 60

CCE was performed in a plastic container under atmospheric pressure, in a water bath with temperature control. After the even distribution of pulp, deionized water and NaOH were added. Mechanical mixing with a mixing blade was applied to ensure even distribution of the chemicals throughout the reaction.

A big batch of CCE treated pulp was produced in a 2-L sealed autoclave with 70 g/L NaOH solution, 30 minutes of reaction time, 5 % consistency and 30 °C. Two batches of 100 g odw pulp were produced. The reason for the selected conditions for scaling up to produce enough pulp for the subsequent bleaching experiment are discussed in the results and discussion.

After the reaction, the residual liquid was separated from the pulp suspension with a nylon filtration bag, and then stored for further analyses. The pulp was then centrifuged to remove the remaining liquid. Thorough washing was conducted with alkaline water (10 g/L NaOH) solution to avoid hemicellulose precipitation due to pH decrease. The washing filtrate was collected for further analysis. Washing was continued with deionized water until the filtrate was at pH 7. Slight yellowness and haze could be observed from the filtrate until the pH was neutral. Washing the pulp aimed to reduce and remove the amount of residual lye and hemicellulose from the pulp.

6.5 Filtrate analysis

Filtrates were collected after CCE and washing. Filtrates were analyzed with TOC analysis according to the SFS-ISO 82-45. Residual alkali content (EA) was determined according to the standard SCAN-N 33:94. The TOC value in pulp filtrates usually represents the carbohydrates and lignin content, and in the scope of the thesis they are considered as dissolved sugars and lignin from the pulp. TOC was determined with SFS-EN 1484 technical standard.

6.6 Carbohydrate analysis

The aim of the carbohydrate analysis is to follow the hemicellulose removal using different process conditions. Carbohydrate analysis was performed with High-Performance Anion-Exchange Chromatography (HPAEC) with Dionex ICS-3000 according to the NREL/TP-510-42618 standard. HPAEC results were calculated with Janson calculation method described by Janson (1970).

6.7 Bleaching

The bleaching sequence D_0-EOP-D_1-P (Figure 19), with the conditions listed in the Table 7 was performed on the CCE-extracted unbleached pulp. EOP was performed in sealed 2-L autoclave with heating, the reactor was flushed and pressured with oxygen. Other bleaching stages were conducted in sealed plastic bags in a temperature controlled water bath. Washing was conducted and filtrate was collected between every stage to follow residual chemicals and to ensure constant bleaching results. The bleaching sequence was ECF bleaching with D_0 and D_1 being the chlorine dioxide stages, EOP the alkaline stage and P the peroxide stage. Process variables that were measured in this stage were temperature, pH, residual chemicals, lye concentration and time. In laboratory conditions, the bleaching was batch-based, but in the pulp mills, the processes are usually continuous.

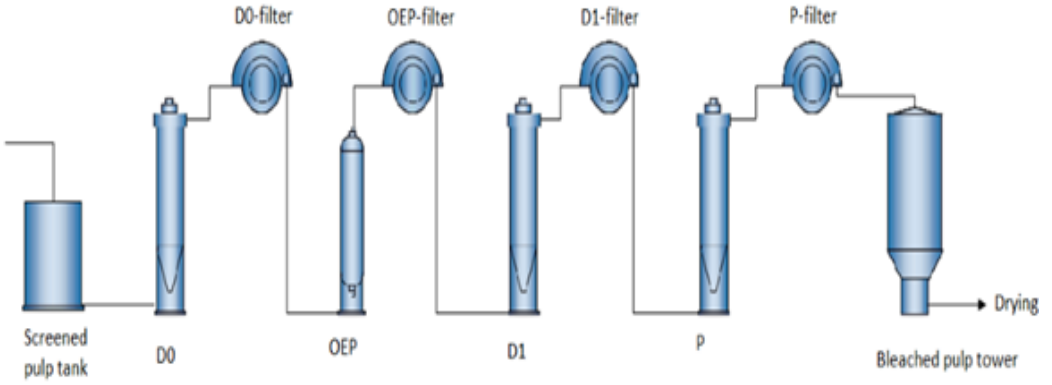

Figure 19. Bleaching process (Stora Enso Internal document, 2019)

Table 7. Bleaching sequence conditions (Stora Enso internal document, 2019)

Property / Stage	D_0	OEP	D_1	P
NaOH [kg/Adt]	-	5	1	5
Pressure [O_2, bar]	-	3.5	-	-
ClO_2, act Cl [kg/Adt]	13	-	11	-
H_2O_2 [kg/Adt]	-	4	-	3
Consistency [%]	10	10	10	10
Temperature [°C]	65	77	78	77
Time [min]	30	60	120	120
final pH	2-3	10.5-11.5	4-4.5	11-11.5

6.8 Carbohydrate loss

Bleaching loss originated from the removal of lignin and hemicelluloses. It can be calculated from kappa number [change of kappa number during reaction] and TOC [% od. unbleached pulp] with Equation 1. (Sixta, 2012) Bleaching loss yields differ from the gravimetric yields since other losses, such as cellulose degradation and loss of pulp might occur in the reaction and in the handling process.

$$BL - L(\%) = (2.25 * TOC - 0.5081 * \Delta\kappa) * 0.1 \quad (1.1)$$

6.9 Acetylation

Acetylation was executed using the method from Rhodia Acetow, described in doctoral dissertation by Testova (2015). Bleached pulp sample was thoroughly mixed with glacial acetic acid until a homogeneous mixture and the excess of acetic acid was removed. Activation acid, the solution of sulphuric acid and acetic acid, was mixed with the pulp. Activation was continued for pre-set amount of time and upon completion, the acetylation process started upon the addition of acetic anhydride. The completion of the activation was visually determined when no bundled fiber was observed, and the pulp had swelled. The acetylation reaction was sustained in a glass reactor at the controlled temperature of 35 °C. The progression of the reaction was monitored with the ball-fall viscosity measurement. Upon reaching the optimum ball fall viscosity, the reaction was terminated with stopping acid (60 % acetic acid containing 2 % sodium acetate). Stopping acid was mixed for set time, and after the mixing, the suspension was cooled in the temperature-controlled water bath. After cooling, the product was analyzed. (Testova, 2014a)

Quality of the CA was analyzed with transmittance, turbidity, yellowness and ball fall viscosity. Transmittance was measured with Turbiscan MA 2000 device. The triacetate solution was prepared in Ø12mm glass tube with 5-minute evacuation in vacuum desiccator. For yellowness measurement, the sample was put into a 10 mm cell and degassed with 5-minute evacuation in vacuum desiccator. The yellowness was measured with Shimadzu UV-2550 spectrometer in wavelengths of 440 nm and 640 nm with reference solution of 10 mL acetic acid, 5 mL activation acid and 5 mL acetic anhydride. The yellowness value (Cy) was calculated with Equation (2.2) and was based on the absorption coefficients. (Testova, 2014a)

$$Cy = \frac{10^{-abs640nm} - 10^{-abs440nm}}{10^{-abs640nm}} \quad (2.2)$$

7 Results and discussion

Results are gathered and discussed in this chapter. The results are divided into sections to clarify the different methods and analyses conducted on the pulp. The summary of the results is presented; the results are then in a chronological order from initial characterization of raw material followed by CCE, bleaching and acetylation.

7.1 Summary of results

CCE test series analysis resulted in choosing the 70 g/L NaOH for the following bleaching and acetylation experiments. The main arguments and reasoning for the decision is cost-effectiveness: after 70 g/L NaOH, xylan content decrease, ISO brightness, viscosity total organic carbon in the solution, macromolecular properties, are not significantly increasing. Literature suggests that 100-120 g/L (Sixta, 2006) would be the optimal value in regards of xylan removal, depending on the temperature, as higher temperature increases the requirement for alkali. Kappa number is decreasing, which is positive, but it should be addressed in cooking or bleaching rather than in the CCE. After CCE 60 g/L for HWBS, the amount of residual NaOH accelerated with increasing concentration of NaOH.

High purity levels could be reached with some of the tested CCE pulps, but all of the criteria, such as viscosity, kappa, hemicellulose content, remained outside of the range of high-quality acetate-grade pulp characteristics. The low initial viscosity induced significant degradation during acetylation of the samples, resulting in a CA solution of a medium or low-grade. To reach improved quality with the same raw material, optimization for the whole process, especially the cooking, is required. Also, for some of the pulps hemicellulose content and kappa number were not on the acetate-grade level, but just above the minimum values.

7.2 CCE test series results

7.2.1 Kappa number

Kappa number analyses of the pulps after CCE in different concentration and temperature are presented in Figure 20. Kappa number of unbleached HWBS decreased from 3.3 to around 1.0. Higher temperature CCE resulted in slightly lower kappa number. Kappa number decrease of HWBS samples followed almost linear correlation with the increase of NaOH concentration with no significant plateauing. The stable decrease of kappa number could be due to reaching maximum amount of xylan and lignin removal in the process conditions. Bleached DPs had already low kappa number of around 0.5 and the kappa number remained stable and relatively unaffected. The temperature does not have a significant effect on the kappa number decrease. Even the most intensive CCE results in greater kappa number of 1.2 for CCE T30 and 0.9 for CCE T60 than the recommended literature value of maximum 0.2 (Sixta, 2006). The kappa number for the bleached pulps are not affected by the CCE treatment, which means that the cooking and bleaching step should also be more intense.

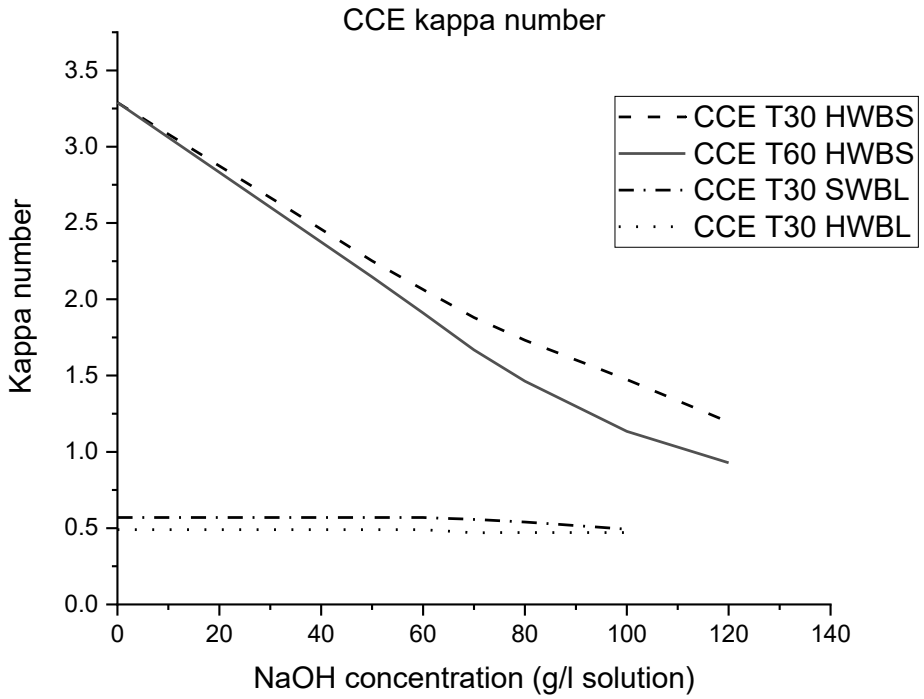

Figure 20. Kappa number of CCE pulps in different temperatures and NaOH concentrations.

7.2.2 Yield and, CCE and carbohydrate loss

The yield loss correlates with the removal of carbohydrates and lignin as presented in Figure 21. In addition, small amount of cellulose degradation of the cellulose chain is decreasing the yield. For the already bleached pulps, the yield reduction is notably lower. No notable difference between SW and HW yield loss was observed. Temperature had slight effect on unbleached pulp yield in lower concentrations, but in higher concentrations after 70 g/L NaOH the difference is marginal.

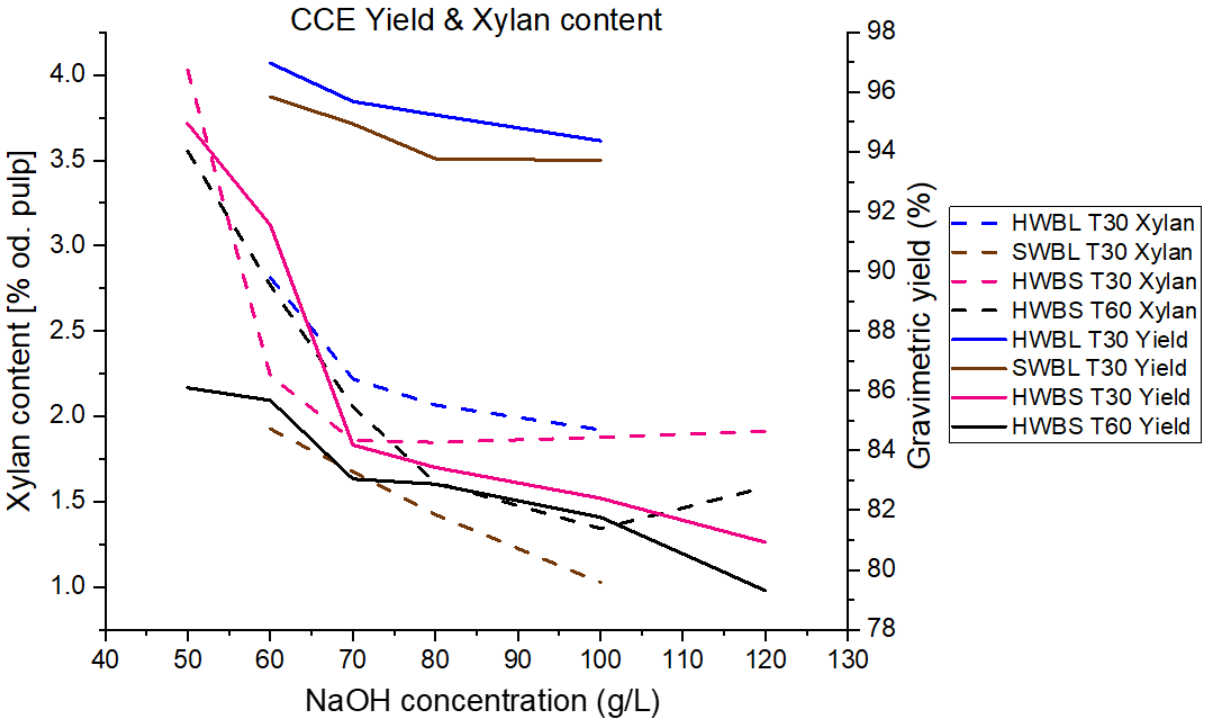

Figure 21. The gravimetrical yield of CCE in different temperatures. Right axis with solid line is for yield and left axis with dashed lines are for xylan content.

7.2.3 ISO brightness

The brightness increased proportionally with NaOH concentration up to a stable level of brightness (Figure 22). In CCE T30, the stable brightness level was around 64 % and in CCE T60 stable level is around 67 %. Maximum value for brightness can be observed after 60 g/L and even slightly decrease after the maximum value when increasing NaOH

concentration. This could be due to the nature of the ISO brightness measurement, where light reflectance properties weaken, when smaller structures are removed from the pulp.

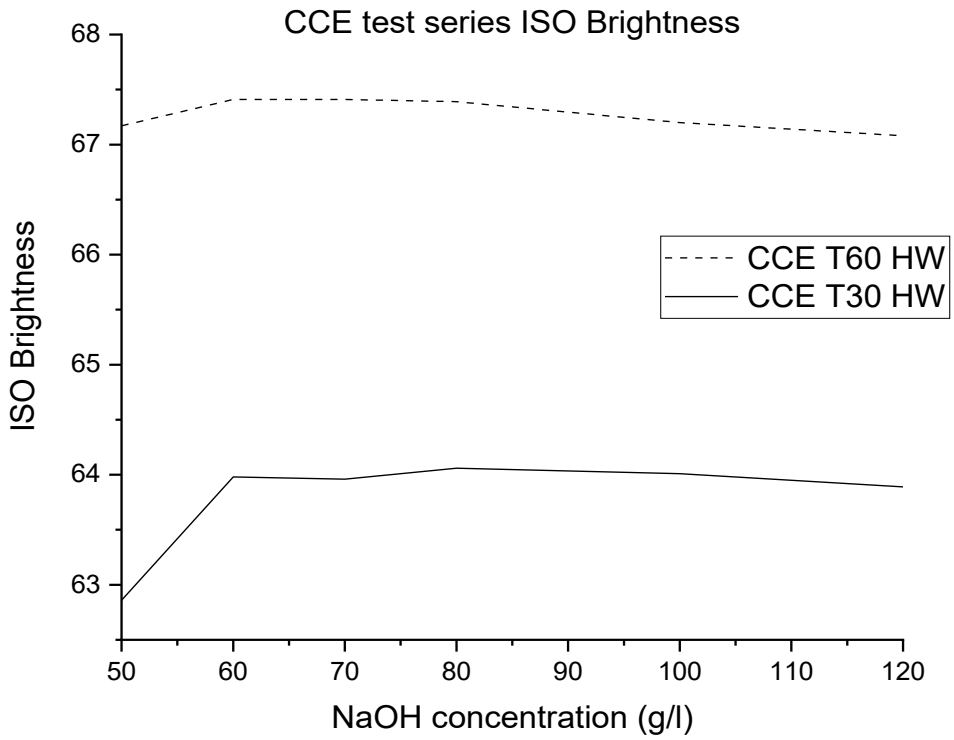

Figure 22. ISO brightness of the CCE HWBS in different temperatures.

7.2.4 Viscosity

Viscosity analyses showed a trend of increasing viscosity, which was nearly linear with the increase of NaOH concentration (Figure 23). Viscosity of the CCE-treated pulps increased due to the low Mw fraction removal, consisting mostly of hemicelluloses and low Mw cellulose. The initial level of HWBS was around 630 mL/g and increased to around 730 mL/g for CCE T30 and to around 640 mL/g for CCE T60. This viscosity trend also followed the removal of hemicellulose. The same trend, but with a lessened intensity was observed from the HWBL (viscosity 475 mL/g to 500 mL/g) and SWBL (390 mL/g to 420 mL/g). Hemicellulose fractions are mainly lower DoP fractions, while cellulose fractions tend to have higher DoP. When the smaller fractions were removed in form of hemicellulose and the higher molecular weight fractions, meaning the cellulose, remain mostly intact, the viscosity increases. Higher temperature showed lower overall viscosity for HWBS samples,

in 60 °C the viscosity remained stable after the initial decrease, as with the 30 °C the increasing trend was clearer. The resulting viscosity for HWBS treated in CCE T30 with 120 g/L NaOH was comparable to the literature reported value of 730 mL/g (Sixta, 2006) for HW PHK acetate-grade pulp. However, after the bleaching, viscosity decreases to around 450 mL/g, which is significantly lower.

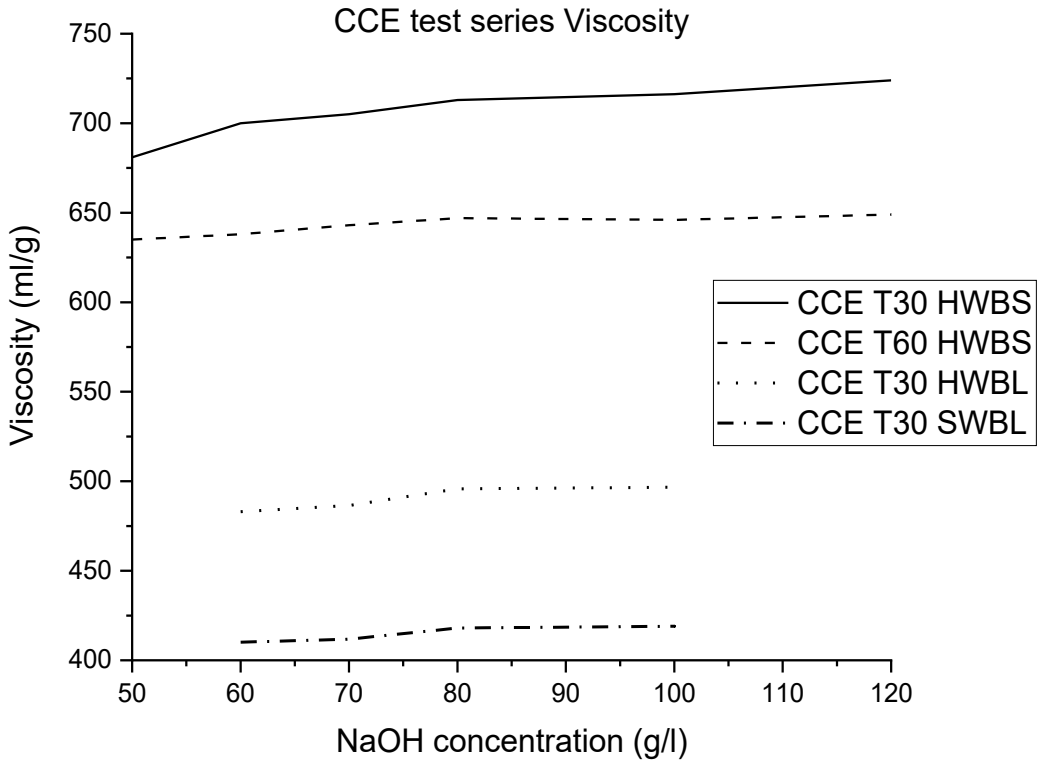

Figure 23. Viscosities of the different CCE test series.

7.2.5 Carbohydrate analysis, TOC, washing

Carbohydrate content analysis showed a steep initial decrease in xylan content, followed by the xylan removal levelling off (Figure 24). From the initial almost 7 % xylan content in HWBS, the first tested NaOH concentration had shown a reduction to almost half of the initial content. After around 80 g/L NaOH, the xylan content was stable, which indicated the maximum xylan removal in the process conditions. The same trend was present in all the HW samples. For SW samples, the reduction of xylan content showed a steady decline

without platforming in the tested conditions. CCE conditions of 70-80 g/L NaOH at both temperatures resulted in around 2 % of residual xylan content, which is slightly higher than the literature recommended 1.5 % hemicellulose content (Sixta, 2006). Under 70 g/L NaOH, the dissolved amount of hemicellulose decreased when increasing the temperature. The TOC does not have as clear of a plateauing trend as the xylan content decrease, which indicated the degradation of the cellulose, while xylan content was stable, as seen from Figure 25. Literature value reported for maximum xylan removal for HW treated with CCE 20 °C is 100 g/L NaOH and in 50 °C around 140 g/L NaOH, and a stable level in around 1 % xylan content after 140 g/L (Sixta, 2006). Treated pulp samples had lower xylan content than those in the literature, but the trend of rapid removal and plateauing was similar regardless.

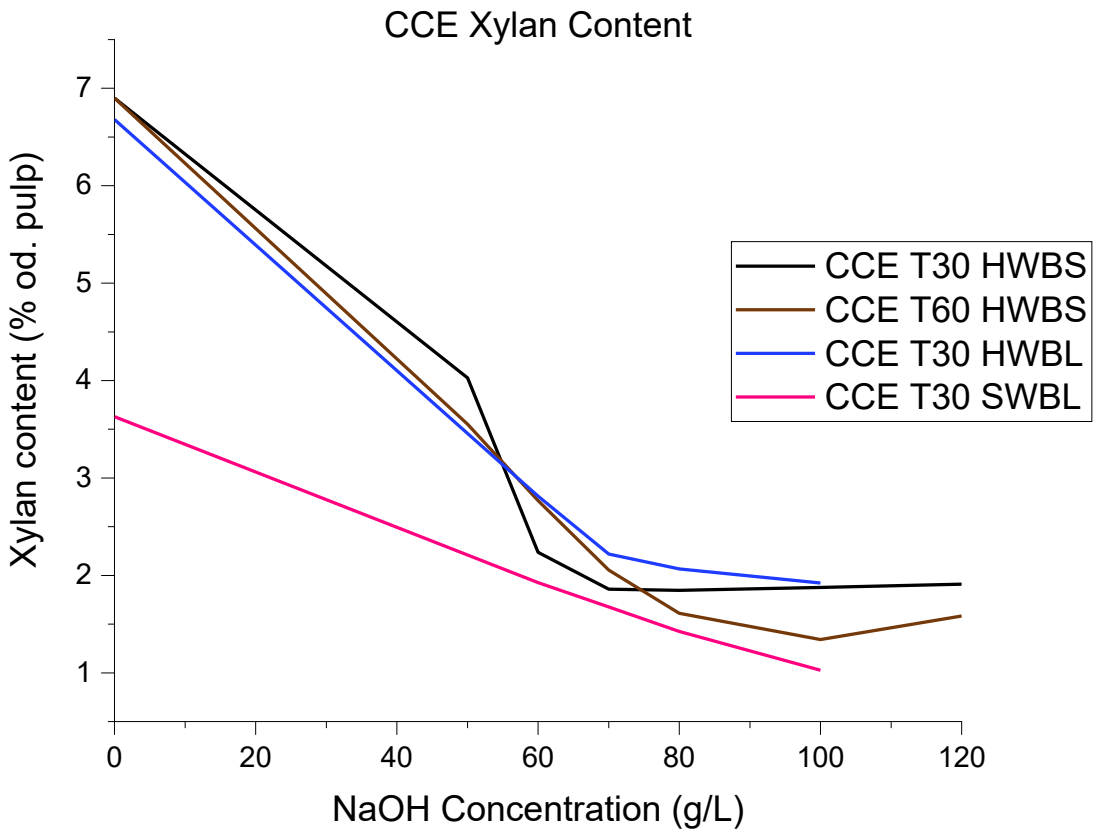

Figure 24. Xylan content of pulp in relation to NaOH concentration.

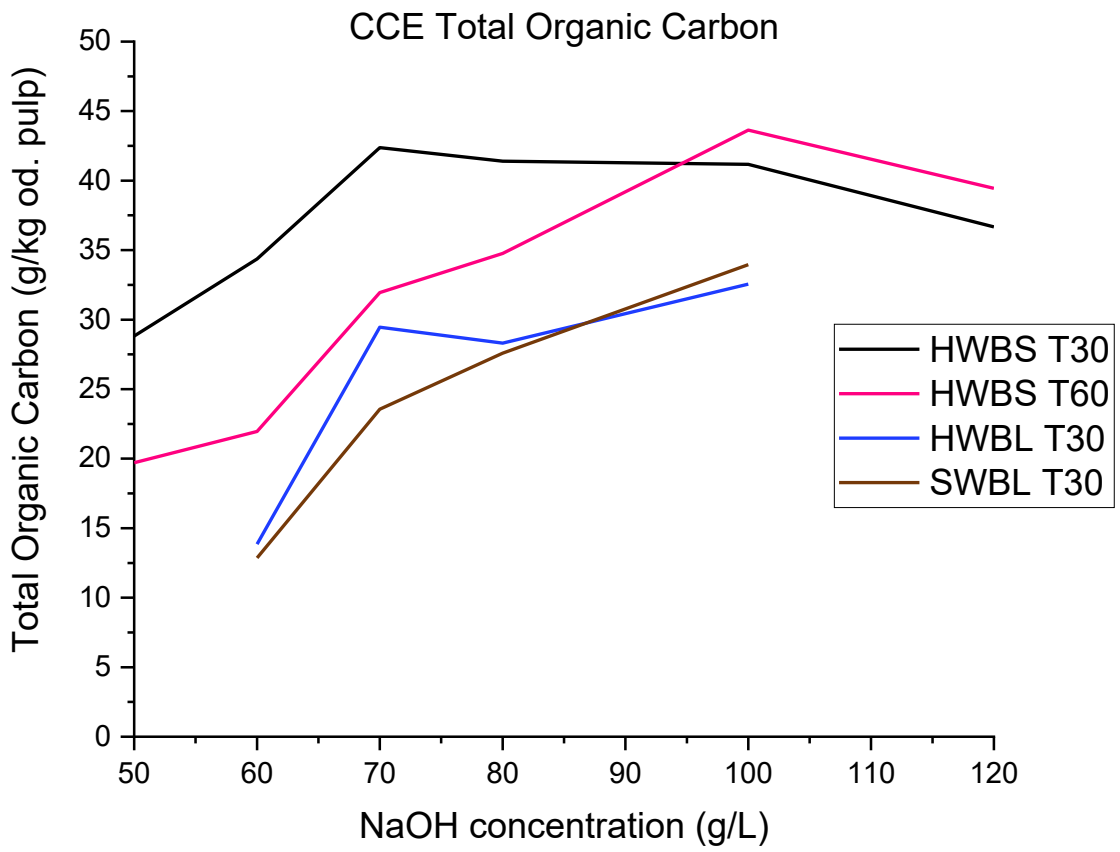

Figure 25. Total organic carbon analysis results in relation to NaOH concentration.

7.2.6 GPC

GPC results showed that the Mw of CCE treated pulps increased as compared to the untreated HWBS (Figure 26). This means that the components with low Mw (DP<100) containing mostly hemicelluloses and degraded cellulose were successfully removed from the pulp. The higher molar mass fractions (DP>2000) remained almost unaffected by the treatment. The higher molar mass fractions contained cellulose fractions with high DoP.

Log 4.21 corresponds to the DoP<100 and Log 5.51 corresponds to the DoP>2000. The intensity of the peak shifted to the right from the original raw material peak, indicating a reduction in hemicellulose content. The shoulder in the low Mw region of CCE120T30 sample indicated the cellulose degradation at higher NaOH concentrations.

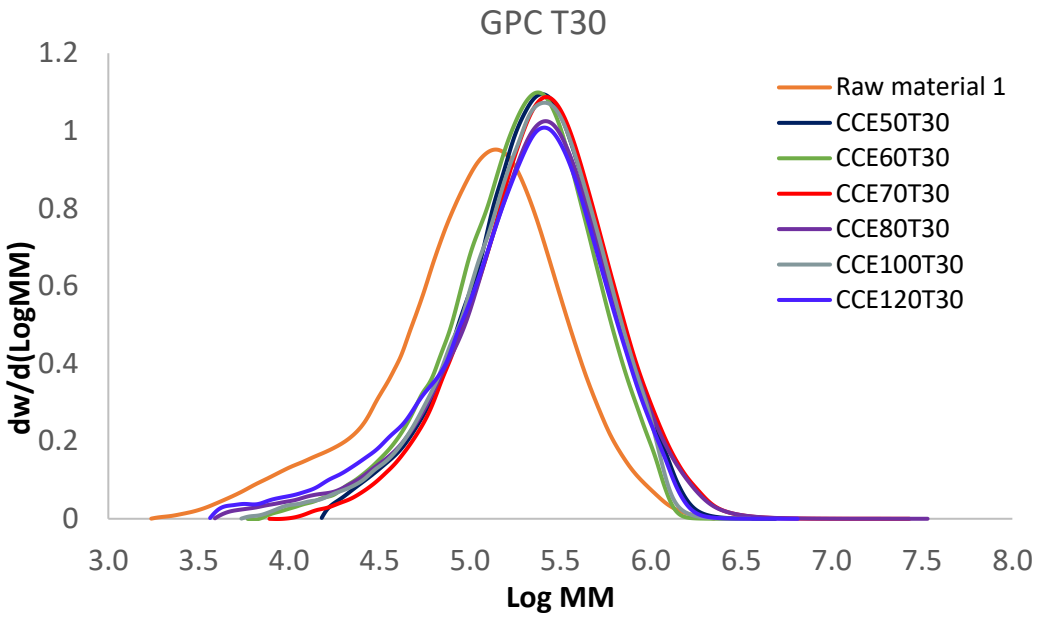

Figure 26. Molar mass distribution of the CCE-treated pulps from HWBS.

A clear increase in high Mw fraction (DoP>2000) was observed from 13 % to 29-35 % comparing the untreated HWBS and CCE treated HWBS samples. Results are slightly lower or similar to than the value for high Mw fraction reported in the literature for HW PHK acetate-grade pulps, which is 35 % (Sixta, 2006). Macromolecular results are presented in the Table 8. The polydispersity index (PDI) decreased in the CCE treatment from 3.6 to 2.2-3.2, yielding similar to or more suitable results for acetate-grade pulp than the literature value for HW PHK acetate-grade pulps, which is 3.2 (Sixta, 2006). Lower PDI values means that CCE is yielding more homogeneous pulp and combining the results with the decreased low Mw fraction (DoP<100). However, the results for low Mw fraction are not uniform ranging from 1.0-2.6 and are even lower than the literature values of 2.0 (Sixta, 2006) for HWBS PHK acetate-grade pulp. Calculated and measured viscosities are on the same vicinity, with difference that calculated viscosity reaches a maximum, while measured viscosity has slight linear increase in the CCE T30 70 g/L NaOH treatment. A major takeaway from the data is that the DoP values change and then reach a certain value and plateauing, with some clear outliers, probably due to data mishandling or unsuitable sample. The plateauing trend is in line with CCE xylan content as well as TOC values, resulting the correlation between increasing the intensity of CCE and decrease of

xylan content being confirmed. However, the plateauing also indicates that increasing intensity of CCE after 70 g/L has negligible effect on DoP improvements, PDI and viscosity.

Table 8. PDI, Viscosity and DoP values of the HWBS test series compared to raw material.

Sample	PDI	DoP<100 [%]	DoP>2000 [%]	Viscosity [mL/g] calculated	Viscosity [mL/g] measured
Untreated HWBS	3.6	6.9	13	680	681
CCE50T30	2.4	2.6	33	710	700
CCE60T30	2.3	1.1	29	740	705
CCE70T30	2.3	1.0	35	760	713
CCE80T30	2.2	2.3	32	740	716
CCE100T30	2.6	1.4	34	730	724
CCE120T30	3.2	1.4	33	720	730

7.2.7 Residual chemicals

Residual chemicals were sampled from the filtrate just after the reaction after which the first wash was performed with 200 mL of deionized water. The samples were analyzed with a standardized procedure to ensure the comparability of the results. Residual chemicals increased with increasing NaOH dosage, as illustrated in Figure 27. Increasing the amount of chemicals increased the amount of unreacted chemicals passing into the filtrate without significantly contributing to xylan removal. The optimal value for these process conditions was 70 g/L NaOH for the HWBS pulp. Beyond 70 g/L, the amount of residual alkali increased without further xylan removal. The residual alkali increase reduces the economic feasibility due to increased alkali usage, resulting in extra costs on chemicals and in the spent liquor treatments.

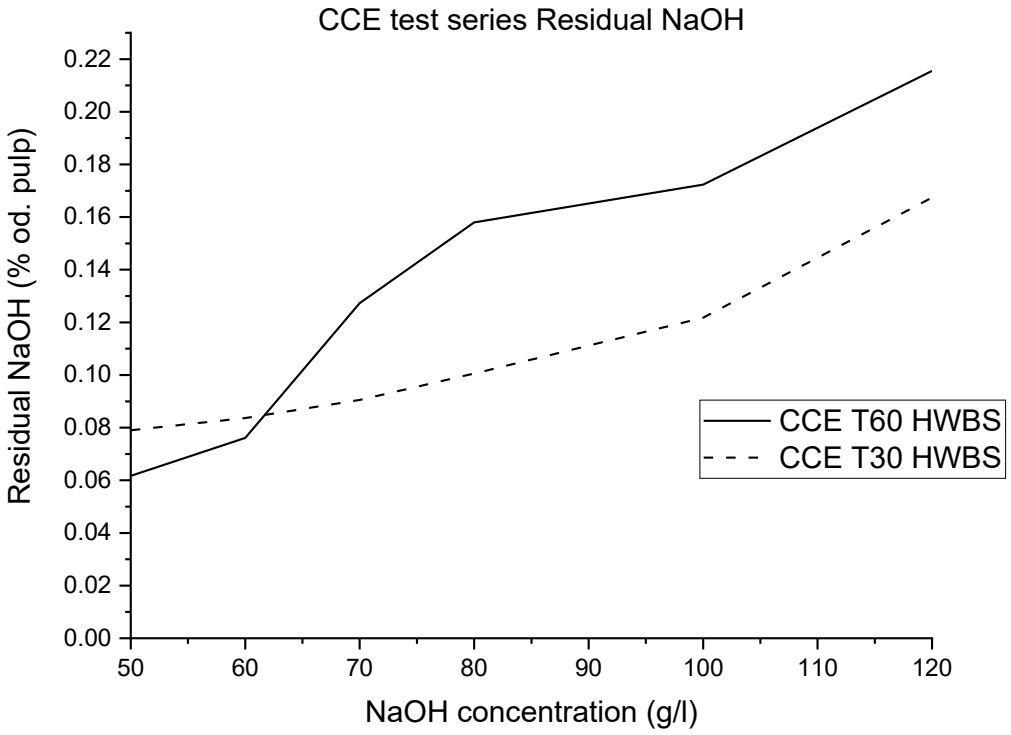

Figure 27. CCE residual alkali in different temperatures and concentrations.

7.3 HWBL, SWBL and HWBS results

HWBL (birch), SWBL (pine), commercial samples of acetate-grade hardwood (HWC) and softwood (SWC), samples were received in dry sheets. The samples were characterized before the CCE test series. HWBL and SWBL were treated with the same test series than for the HWBS, however, the extremities of 50 g/L NaOH and 120 g/L NaOH were left out of the series for the mill bleached pulps based on the experience from previous experiments. The results are presented in the Table 9 & 10 (HWBS), Table 11 (HWBL) and Table 12 (SWBL). For comparison, commercial acetate-grade pulps are presented in Table 13. The most important property is the hemicellulose content of the pulp, since it is the milestone for purification of the pulp and is related to TOC, losses, viscosity and yield.

Table 9. HWBS samples CCE test series results in 30 °C.

Material / Property	κ	TOC [mg/L]	Xylan [% odp]	Yield [%]	η [mL/g]	CCE Loss [%]	Res. NaOH [% odp]
HWBS	3.3	-	6.9	100	632	0	0
CCE50T30	2.3	1080	4.0	94.9	681	6.4	7.9
CCE60T30	2.1	1440	2.2	91.6	700	7.7	8.4
CCE70T30	2.0	1700	1.9	84.2	705	9.5	9.1
CCE80T30	1.9	1620	1.9	83.4	713	9.2	10.1
CCE100T30	1.7	1810	1.9	82.4	716	9.2	12.2
CCE120T30	1.7	1630	1.9	80.9	724	8.2	16.7

Table 10. HWBS samples CCE test series results in 60 °C.

Material / Property	κ	TOC [mg/L]	Xylan [% odp]	Yield [%]	η [mL/g]	CCE Loss [%]	Res. NaOH [% odp]
HWBS	3.3	-	6.9	100	640	0	0
CCE50T60	2.0	570	3.6	86.1	635	2.3	6.2
CCE60T60	2.0	780	2.8	85.7	638	3.1	7.6
CCE70T30	1.5	1090	2.1	83.0	643	4.2	12.7
CCE80T30	1.4	1200	1.6	82.9	647	4.6	15.8
CCE100T30	1.5	1630	1.3	81.8	646	6.2	17.2
CCE120T30	1.7	1690	1.6	79.3	649	6.2	21.6

Table 11. HWBL samples CCE test series results.

Material / Property	κ	TOC [mg/L]	Xylan [% odp]	Yield [%]	η [mL/g]	CCE Loss [%]	Res. NaOH [% odp]
HWBL	0.5	-	6.7	100	475	0	0
CCE60T30	0.5	1370	2.8	97.0	483	3.1	8.4
CCE70T30	0.5	2800	2.2	96.7	486	6.6	10.2
CCE80T30	0.5	2740	2.1	95.2	496	6.4	10.7
CCE100T30	0.5	3240	1.9	94.4	497	7.3	13.1

Table 12. SWBL samples CCE test series results.

Material / Property	κ	TOC [mg/L]	Xylan [% odp]	Glucomannan [% odp]	Yield [%]	η [mL/g]	CCE Loss [%]	Res. NaOH [% odp]
SWBL	0.6	-	3.6	3.0	100	392	0	0
CCE60T30	0.6	1220	1.9	2.8	95.8	410	2.9	8.1
CCE70T30	0.6	2200	1.7	2.4	94.9	412	5.3	9.2
CCE80T30	0.5	2600	1.4	2.1	93.8	418	6.2	9.6
CCE100T30	0.5	3230	1.0	1.4	93.7	419	7.6	12.7

Table 13. Commercial acetate-grade pulp properties.

Material / Property	κ	Xylan [% odp]	Glucomannan [% odp]	ISO B. [%]	η [mL/g]	PDI	R_{18}
HWC	0.2	1.8	0.2	91	585	3.4	96.9
SWC	0.2	0.8	0.7	91	918	5.3	98.1

None of the non-commercial samples reached the under the literature suggested 1.5 % (Sixta, 2006) hemicellulose content, or kappa of 0.2 (Sixta, 2006) with any of the process conditions. However, HWBS CCE T30 after 70 g/L, HWBS CCE T60 after 80 g/L NaOH and HWBL CCE T30 after 100 g/L nearly matched the hemicellulose content of the HWC sample with 2 % combined hemicellulose content. SWBL purification failed to reach under 2 % hemicellulose content in any of the tested conditions. The viscosities of the samples were also significantly lower than the viscosity of the commercial samples.

7.4 Big Batch results analysis

Certain deviation was observed in the properties of the pulp produced in the bigger and smaller scale (Table 14). The resulting higher xylan content was the main difference, which could be explained by inferior reaction conditions in the 2-L autoclave as compared to the blade-mixing in smaller scale experiments. However, since the kappa number was lower, but xylan higher, disturbance was caused by the reactor as well. The main difference in the reaction conditions was atmospheric pressure when producing smaller batches and

sealed reactor when producing bigger batch. Similar remarks are observed from the big batch than the CCE test series counterpart, since they did not reach the literature suggested values on most of the criteria. However, the R_{10} and R_{18} measured for the big batch of 97.4 and 98.5, respectively, reached the literature value of R_{18} for ECF bleached HW PHK of 98.2 (Sixta, 2006), but slightly missed the R_{10} value of 97.7 (Sixta, 2006).

Table 14. CCE Big batch in reactor with 70 g NaOH / L solution at 30 °C.

Property	**Big Batch CCE70T30**	**CCE70T30**
Kappa number	1.20	1.88
Xylan content [% odp]	2.70	1.86
TOC – Process/wash filtrate [mg/L]	1520 / 230	1540 / 162
Gravimetric yield [%]	83.5	84.2
ISO Brightness [%]	63.6 ± 0.3	64.0
CCE loss [%]	7.8	9.5
Ash [% odp]	0.16	0.14
Viscosity [mL/g]	696 ± 10	705 ± 10
Residual NaOH [%]	10.8	9.0
S_{10} / S_{18} [%] calculated	4.8 / 1.8	n.m.
R_{10} / R_{18} [%] gravimetric	97.4 / 98.5	n.m.

Abbreviation n.m. = not measured.

The big batch of CCE HWBS was bleached and the bleached pulp properties are summarized in Table 15. The residual chemicals, ISO brightness and yield were on a good level, indicating a bleaching is working efficiently. However, ash content of 0.18 % is higher than the literature suggested value of 0.07 % (Sixta, 2006) for acetate-grade hardwood pulps. The viscosity drops in D_1 and P were significant, which is disadvantageous for CA-grade pulps as higher viscosity is preferred. This reduction of viscosity could be reduced with the addition of EPSOM salt ($MgSO_4$). As expected, the xylan content is almost unaffected by the bleaching procedure.

Table 15. Bleaching results of the HWBS in different stages. (odp: oven-dried pulp)

Property / Stage	ISO [%] Brightness	η [mL/g]	Xylan [% odp]	Residual ClO_2 [%]	Residual H_2O_2 [%]	Yield [%]	Ash [%]
D0	75.3 ± 0.7	683 ± 10	2.9	0.30	n.m.	n.m.	n.m.
EOP	86.0 ± 0.1	652 ± 15	2.6	n.m.	0.82	n.m.	n.m.
D_1	89.0 ± 0.1	560 ± 10	2.7	0.10	n.m.	n.m.	n.m.
P	90.3 ± 0.2	451 ± 15	2.6	n.m.	0.30	94.9	0.18

Abbreviation n.m. = not measured.

7.5 Acetylation results

The acetylation results, including turbidity, ball fall viscosity and UV spectroscopy measuring yellowness are presented in Table 16.

First, high-quality acetate-grade market pulps (HWC & SWC) were acetylated to establish benchmark to compare with the acetylation of the CCE pulps. DoP mill bleached samples of CCE 70 g/L NaOH in 30 °C, HW 1 and SW 1, were left to acetylate until the viscosity remained constant, indicating the completion of acetylation. The acetylation of samples HW 2 and SW 2 (milled bleached samples treated in 100 g/L NaOH at 30 °C) were terminated when the ball-fall viscosity was too low, despite the acetylation visually not complete (high haze). The acetylation of samples HW 3 and SW 3 (mill-bleached samples treated in 70 g/L NaOH at 30 °C) were terminated when ball-fall viscosity of 30 seconds was achieved, which resulted in mixed results. SW 3 pulp can be seen to result in a complete reaction as seen from the results. HW 3 pulp reaction was not complete, which can be deducted from the low transmittance. The treatment of HWBL 4 and SWBL 4 were prolonged to ensure a complete acetylation. The resulting solutions had negligible transmittance and low viscosity, while having reasonable yellowness.

Table 16. Acetylation results of the different pulps.

Property / Sample	[NaOH g/L]	Transmittance [%]	Ball fall viscosity [s]	Yellowness	Acetylation time [min]
HWC	-	78	40	0.27	100
SWC	-	73	45	0.35	80
HWBLBS	70	18	28	0.38	45
HWBL 1	70	50	19	0.29	124
HWBL 2	100	3	26	0.19	15
HWBL 3	70	17	28	0.30	98
HWBL 4	100	0	10	0.28	240
SWBL 1	70	39	21	0.24	119
SWBL 2	100	3	29	0.13	31
SWBL 3	70	40	29	0.26	101
SWBL 4	100	0	11	0.26	210

The yellowness coefficient for CA produced from SW and HW PHK pulps should be ranging from 0.2-0.5 for pulps with xylan content of roughly 1-3 % (Sixta, 2006), respectively. The yellowness coefficient correlates fairly well with the literature values, with HWBL 2 and SWBL 2 being outliers. Commercial samples had relatively long acetylation times, as they were expected to be highly reactive. Literature value for commercial PHK hardwood pulp was reported to have 30-minute acetylation time (Testova, 2014b). Most of the samples did not react properly, or they were not suitable for acetylation, since the literature values for viscose and acetate-grade pulps were 77 % and 82 % (Testova, 2014b), respectively.

Purity of the HWBL and SWBL were high, but the viscosity and acetylation were not adequate for CA production. The high purity was achieved by the CCE treatment as demonstrated by the reasonable yellowness values. No pulp was properly acetylated, as proven by low transmission values. Additionally, the measured ball fall viscosity was under the critical value for suitable viscosity. For the higher NaOH concentrations and shorter reaction times, very low transmittance was observed. Low transmittance indicates that the pulp could be too degraded and thus not react properly. However, the low viscosity causes the reaction to be stopped early if the acetylation procedure is followed, which was observed from low transmittance values in some of the reactions due to the

acetylation not being complete. The mill bleached pulps had low initial viscosity. When increasing the intensity of the CCE purification beyond the 70 g/L NaOH to a certain extent, the acetylation results began to deteriorate with the tested pulps.

For the later tests, acetylation times were extended, and the ball fall viscosity was ignored, which resulted in far better transmittance values and confirmed the possibility to produce medium-quality CA from 70 g/L NaOH CCE bleached HW and SW pulps. The SWBL acetylation had reasonable results, but more optimization is needed since the results might have been past the optimal transmittance values. However, the possibility of reaching the process condition optimum was also achieved as the SWBL 1 and SWBL 3 resulted in nearly identical results with different optimizations. The acetylation reaction conditions worked slightly better for the lower concentration CCE HWBL pulp. The HWBL 1 with ignored ball fall viscosity resulted in the best transmittance value.

7.6 Sources of errors

All the experiments were performed in at least duplicate. The variation can result from analysis method, equipment variation, pulp quality, varying conditions in laboratory or handling error. The experiments were performed as batch processes, unlike in the pulp mill, where the process is continuous. The acetylation reaction conditions were designed for higher viscosity pulp, which lead to high reactivity and it is probable that at some experiments complete cellulose acetylation was rapidly achieved and subsequently undesired cellulose degradation occurred.

8 Conclusions

Upgrading delignified birch PHK dissolving-grade DP to acetate-grade with CCE treatment was researched. Applying moderate to intense CCE resulted in relatively pure pulp with unsuitable properties for acetate-grade pulp. A cost-effective option was chosen to subsequent bleaching and acetylation processes. Treated pulp was successfully bleached and acetylation was attempted, with unsatisfactory results. Mill bleached pulps were also treated with CCE, followed by acetylation. In each of the tested pulps, the resulting CA had suboptimal properties, which was probably due to low DoP, relatively high hemicellulose content and unoptimized acetylation process.

Intensifying the CCE treatment of the pulps increased the xylan removal, brightness, viscosity, the amount of residual chemicals, but also decreased kappa number and yield. Most of the improved properties contributed towards upgrading the pulp, but acetate-grade was still not reached since some plateauing was observed in the process conditions in at least xylan removal, kappa and brightness as the intensity of the CCE treatment conditions increased. The plateauing trend inherently indicates the maximum values in current process conditions, resulting in requirement for further research with the raw material and process conditions.

Intense removal of hemicelluloses and lignin during CCE treatment can cause cellulose degradation in subsequent bleaching stages, since bare cellulose fibers are susceptible to peeling reactions without the protective layer of hemicelluloses or lignin, causing viscosity drop. If bleaching is performed after CCE, the intensity of the bleaching should be adjusted accordingly. After the laboratory bleaching, viscosity levels were low, resulting in a negative effect on the acetylation results.

Overall, the materials did not seem suitable for production of acetate-grade pulp, and subsequently the resulting CA was low-quality when comparing to the market acetate-grade pulps and their corresponding acetylation results. Further optimization of the different process steps, especially cooking and bleaching, should be further researched.

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Appendices

Appendix 1. Metal analysis of raw material pulps.

Sample name				Pure Birch, HW-BL	SWDP3 Pure, SW-BL	Unbleached Pure, HW-BS	BS Pure, CCE + lab bleaching
Analysis	Parameter	Unit	Standard				
Al	Al	mg/kg dry matter	Mod. ISO 17812	1,2	1,4	1,1	1,3
Fe	Fe	mg/kg dry matter	Mod. ISO 17812:	1,5	2,7	1,9	3,6
Mn	Mn	mg/kg dry matter	Mod. ISO 17812:	0,35	0,53	26	<0.1
Ca	Ca	mg/kg dry matter		51	59	1100	520
Cu	Cu	mg/kg dry matter	Mod. ISO 17812:	<0.25	<0.25	4,2	5,1
Mg	Mg	mg/kg dry matter		7,7	11	57	31
Na	Na	mg/kg dry matter		370	350	470	110
Si	Si	mg/kg dry matter		4,7	6,3	15	11
Cr	Cr	mg/kg dry matter	Mikroaaltoavusteine	0,05	0,11	<0.05	0,07
Ni	Ni	mg/kg dry matter	Mikroaaltoavusteine	<0.15	<0.15	<0.15	<0.15
K	K	mg/kg dry matter		9,9	16	66	39
SiO2	SiO2	mg/kg dry matter	Mod. ISO 17812:	0	0	0	0
Zn	Zn	mg/kg dry matter		1,9	2,4	7,3	3,3